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INDIAN AGRICULTURAL
RESEARCH INSTITUTE, NEW DELHI

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JOURNAL

OF THE

University of Bombay

[PHYSICAL SCIENCES, INCLUDING MATHEMATICS: No. 5]

VOL. V

SEPTEMBER 1936

PART II

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ON THE POLYGONS FORMED WHEN ANY LIQUID-SHEET BREAKS UP INTO CELLS.

By

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It is well known that a liquid and generally fluids whose denser layer lies on the top of a relatively dense layer breaks up into symmetrical polygonal cells provided the density difference is not too great. The regular polygons are obtained when there is no relative shear in the fluid. Several authors have obtained the maximum density difference that can exist before unstable conditions break up the structure. This aspect of the problem is not considered here. The mechanism of cell formation is also not considered. The geometry of the problem is alone dealt with.

The boundaries are supposed to be so distant that they do not exercise any influence on the cellular formation. The disposition of the cells may be taken, without loss of generality, to be the possible symmetrical areas included by lines drawn on a plane. As symmetry is needed and all areas are similar and of equal size, these lines may be assumed to be portions of straight lines. The polygons are formed by the various lines meeting one another. As symmetrical polygons are needed, the polygons should be regular.

If two straight lines meet at a point, symmetry would require that they should be inclined at two right angles (180°). In this case a series of equidistant parallel straight lines are obtained. If three lines meet at a point, symmetry would require them to be inclined at 120° to one another and the polygon with this angle is a regular hexagon. Corresponding to four and six lines meeting at a point, the polygons obtained are squares and equilateral triangles. For any other number of lines meeting symmetrically at a point, it is not possible to have a regular polygon with that angle.

Hence, it may be concluded that so long as the whole area is covered with regular polygons the only possible configurations are—

- (1) equidistant parallel bands,
- (2) regular hexagons,

(3) squares,
and (4) equilateral triangles.

In any actual experiment, however, the conditions obtained are not ideal and degenerate figures can result.

Received 12th August, 1936.

ON THE INTENSITY OF MULTIPLE REFLECTIONS AT A GRAZING ANGLE FROM A NEARLY PARALLEL PLATE

By

(The late) K. T. KADABA & S. L. MALURKAR

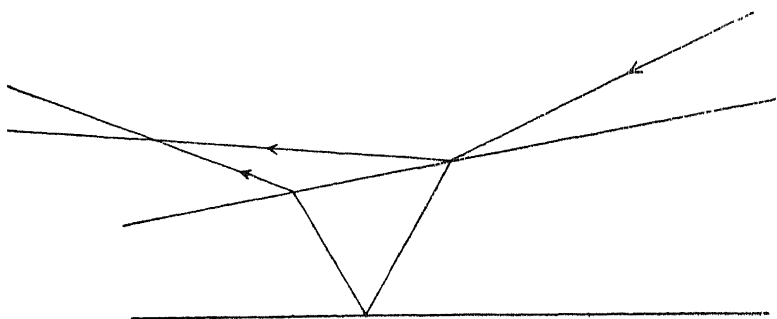
Upper Air Observatory, Agra.

The phenomena of multiple reflections from a parallel plate has been studied in great detail. But there is a simple application of the problem which, perhaps, is not well known. A plate whose surfaces are inclined at a small angle—a portion of a good plate glass will do—is held near the eye and a distant source of light observed so that the reflection is at a grazing angle. Among the many images of the source that are observed, one image is the brightest and others are successively less bright. If now the glass plate is rotated in its own plane and the reflected images are continued to be observed, it is found that the brightest image remains at about the same position while the other images describe closed curves round the brightest image. If the plate is so held that all the reflected images are in one vertical plane, the brightest image is either the topmost or the bottommost one. It may be supposed that the topmost is the brightest image. The other images successively diminish in intensity from top downwards. If the plate is rotated by 180° in its own plane, the reflected images are still in one vertical plane but the intensity of the images decreases from down upwards.

The explanation is very simple. As the reflection is nearly at a grazing angle the brightest image is due to reflection from the top surface of the plate. The other images have undergone two refractions and several internal reflections. The image corresponding to the ray which has had more internal reflections is fainter than the image corresponding to the ray with a lesser number of internal reflections.

The figure (p. 6) shows the reflected ray and the emergent ray after one internal reflection when the incident ray is from the thicker side of the plate. In this case it is easy to see that the successive emergent rays are more and more inclined to the top surface of the plate and hence corresponding images appear lower in the vertical plane. When the incident ray is from the thinner side of the plate the successive emergent rays, corresponding to every increase in internal

reflection, are less and less inclined to the top surface of the plate and hence the corresponding images appear higher in the vertical plane and the brightest image appears lowest. When the incident ray and the line of greatest slope and the normal at the point of incidence are not in one plane the images will be slanting from the vertical and the description of the closed curve will be obvious.



The above phenomenon may be of some use when picking up sufficiently good glass plates for any purpose. The change of the order of intensity of the images can easily be detected by the eye. Once the eye has some training any distant sharp object would be sufficient instead of a light. The method requires practically no equipment other than what is available almost anywhere.

Received 12th August, 1936.

SOME CHARACTERISTICS ASSOCIATED WITH THE CONSTANTS OF THE DIATOMIC HALOGEN AND ALKALI MOLECULES

By

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(With 2 Text Figures.)

Considerable interest attaches to the band spectroscopic constants on account of the periodicity which occurs between them in relation to the structure of molecules. In the field of diatomic molecules alone, we are at present in possession of large experimental material which is used by different authors in putting forth various empirical relations, hypotheses or theories. In these molecules which are considered to be the simplest to deal with mathematically, the methods of spectroscopy have yielded very important information such as the equilibrium distances in different electronic states, the vibration frequency and the dissociation energy. These constants with the help of wave-mechanics have led us to derive relations which are useful to some extent in the elucidation of the chemical properties such as the nature of valences, the occurrence of isomers or the rotation of radicals round a chemical bond. While the theory has far advanced in the case of diatomic molecules so as to give us quantitative agreement with experiment, such is not the case with polyatomic molecules. For the latter, the theory and experiment are more or less in qualitative agreement. This is due to involved nature of connected mathematical problems, the solution of which is rendered difficult on account of the absence of a defined axis of symmetry for the rotation of molecule as a whole. However, considerable progress on the experimental side has been achieved through the observation of pure rotation spectra, vibration-rotation spectra and the Raman effect. The electronic bands for tri- and polyatomic molecules have not been observed except in a few rare cases, probably on account of the dissociation which sets in during the process of excitation. The spectroscopic data obtainable at ordinary temperatures is therefore the only information on which we can base any physical theories. Due to the small energy possessed by these molecules at such temperatures, the derived spectroscopic constants refer only to the ground state

of a molecule. For diatomic molecules, on the other hand, a number of excited states has been identified due to the development of the theory of electronic band spectra and the technique of spectroscopy.

To take some instances of the way in which the molecular constants can be interpreted in relation to their electronic configuration, we can refer to the following relations :

(1) It is known that in diatomic hydrides, the internuclear distance r is one of the additive properties. This quantity increases with the atomic number, becoming larger for hydrides of elements in the same column of the periodic table due to increase in the atomic radius. But for elements in the same horizontal line of the periodic table, the distance r decreases continually upto the inert gases at which discontinuities occur. This diminution of distance is attributed in chemistry to the hardening of molecule.

(2) The nuclear vibration frequency in the case of diatomic oxides has been found to vary with the atomic number in such a way as to cause strengthening upto the middle of a period, where loosening sets in and this continues upto the inert gases.

(3) The binding constants which express the energy required to double the internuclear distance are in the case of hydrides a function of the atomic number of the atom combining with hydrogen to form a physically stable molecule. Here again the discontinuities occur at inert gases.

(4) The binding energy is constant for a group of molecules chemically alike for they have the same number of valency electrons. This can be seen in the case of hydrogen halides where the vibration frequency and nuclear distance alter in spite of the binding energy remaining constant. Alkali molecules also exhibit the same quality.

In the present paper, it is proposed to pursue further the subject of the correlation of constants for some groups of analogous molecules. The symmetric and unsymmetric halogen and alkali diatomic molecules have been chosen for this purpose. They have been found to be sufficient in number to express some general characteristics. All these molecules will be considered in their ground states for the data available is meagre for higher states.

1

THE HALOGEN GROUP

The values of nuclear vibration frequencies* accepted for sym-

* These values are inexact or doubtful for reasons of the inaccuracy of coefficients X_e and α or otherwise. Those in parenthesis represent accurate values. All values are taken from Kronig's 'Optical Basis of the Theory of Valency.'

metric molecules of this group are shown below in Table I.

TABLE I.

Molecule	Reduced Mass $M \cdot 10^{24}g.$	ω_e cm. ⁻¹
Cl ₂	28.86	564.9
Br ₂	65.89	323.86
I ₂	104.65	214.26

For the unsymmetric molecules like IBr, ICl or BrCl we can derive the nuclear frequencies roughly in the following manner, by taking the help of figures in the third column above.

For our purpose we can consider the molecule BrCl to be formed out of Cl₂ and Br₂. If ω_{Cl} is the vibration frequency of Cl₂ and ω_{Br} that of Br₂ the frequency of BrCl is

$$\begin{aligned}\omega_{BrCl} &= \frac{1}{2} (\omega_{Cl} + \omega_{Br}) \\ &= \frac{1}{2} (564.9 + 323.86) \\ &= 444.38 \text{ cm.}^{-1}\end{aligned}$$

Similarly,

$$\begin{aligned}\omega_{ICl} &= \frac{1}{2} (\omega_I + \omega_{Cl}) \\ &= \frac{1}{2} (564.9 + 214.2) \\ &= 389.6 \text{ cm.}^{-1}\end{aligned}$$

and

$$\begin{aligned}\omega_{IBr} &= \frac{1}{2} (\omega_I + \omega_{Br}) \\ &= \frac{1}{2} (323.86 + 214.26) \\ &= 269.06 \text{ cm.}^{-1}\end{aligned}$$

The known and calculated values are compared below.

TABLE II

Molecule.	Calculated ω_e	Known ω_e
ClBr	444.38 cm. ⁻¹	421 cm. ⁻¹
ICl	389.6 "	384.6 "
IBr	269.06 "	(268.4) "

THE ALKALI GROUP

The known nuclear frequencies of this class of symmetric molecules are recorded below.

TABLE III

Molecule.	Reduced Mass M. 10^{24} g.	ω_e cm. ⁻¹
Li ₂	5.771	351.6
Na ₂	18.96	159.2
K ₂	32.15	92.6
Cs ₂	109.50	41.99

Calculations for vibration frequencies of unsymmetric molecules can be carried out in the manner shown above for halogens. These are compared below with the accepted values.

TABLE IV

Molecule.	Known ω_e	Calculated ω_e
LiK	207	222
LiCs	167	196
NaK	123.3	125.9
NaCs	96	100.6

No serious interpretation can be put on these results in view of the inaccuracy involved in the known values of the nuclear frequencies. As the coincidences appeared to be of more than cursory interest, it seemed interesting to record them here.

Other cases in which this relation nearly holds are :

C₂ 1641.55 cm.⁻¹

P₂ 780.4 „

CP 1239.67 „ Calculated $\omega_e = 1211$ cm.⁻¹

and

S₂ 727.4 cm.⁻¹

O₂ 1568.33 cm.⁻¹

SO 1123.73 „ Calculated $\omega_e = 1147.8$ cm.⁻¹

2.

Birge and Mecke⁺ have shown that the quantity B_e / ω_e is constant for different electronic states of the same molecule and varies with the reduced mass for some groups of analogous molecules. Attempt has been made here to calculate this quantity for the groups of halogen and alkali molecules and draw a relation between it and the reduced mass of the molecules. The relation for the halogens has been graphically shown below.

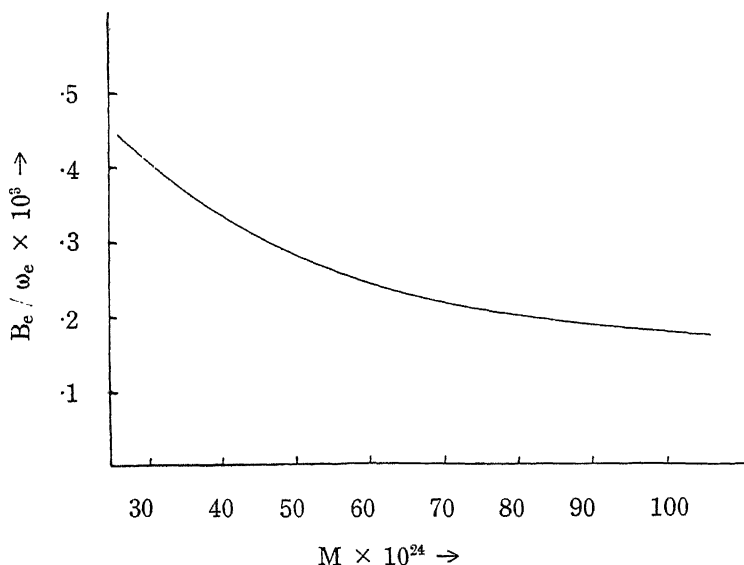


FIG. I

The values of B_e are not known for certain halogen molecules. For such molecules, we can, by means of the above graph, derive the value of B_e by taking the known values of their nuclear frequencies. This allows us to determine their nuclear distance ρ_e from the following relation :

$$B_e = \frac{h}{8\pi^2 M \rho_e^2}$$

For the sake of uniformity only, such calculated values of ρ_e are given below side by side with other constants such as the reduced mass and the number of electrons in the configuration. Those shown in the parenthesis are from the table of constants.†

* Zeit. f. Physik. 32, 823 (1925).

† Kronig's Optical Basis of the Theory of Valency, 1935, pp. 102-103.

TABLE V

Molecule.	No. of electrons.	B_e / ω_e $\times 10^3$	M. 10^{-4} g.	ρ_e^0 Å
Cl ₂	34	.415	28.86	2.016 (1.98)
BrCl	52	.333	40.46	2.214
ICl	70	.299	45.24	2.25 (2.31)
Br ₂	70	.251	55.89	2.326 (2.28)
IBr	88	.209	80.87	2.462
I ₂	106	.174	104.65	2.602 (2.66)

In a similar way the relation between B_e / ω_e and the reduced mass for the alkali molecules has been shown below.

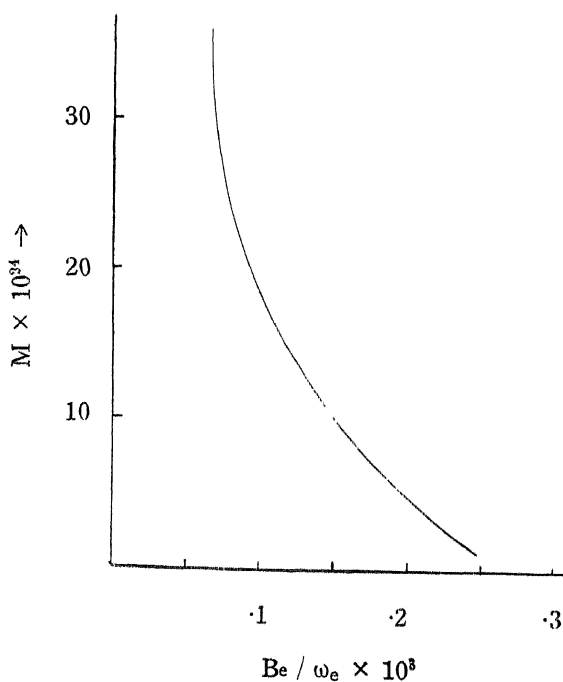


FIG. 2

The values of ρ_e computed from the above graph are given below after the manner of halogens.

TABLE VI

Molecule.	No. of electrons.	$B_e/\omega_e \times 10^3$	M. 10^{24} g.	$\rho_e \text{ \AA}$
Li ₂	6	1.91	5.77	2.66 (2.67)
LiK	22	1.51	9.79	2.99
Na ₂	22	.94	18.96	3.063 (3.07)
NaK	30	.85	23.88	2.94
K ₂	38	.65	32.15	3.907 (3.91)
LiRb	40	1.47	10.67	3.077
LiCs	58	1.45	10.97	3.215
NaCs	66	.64	32.33	3.748

Assuming that our relation $B_e/\omega_e : M$ holds in each of the groups of molecules considered, it becomes evident from the above results that as far as the halogen molecules (Table V) are concerned, there is regularity between the different quantities such as ρ_e (computed) depending upon the reduced mass and the number of electrons in the molecular configuration. Such is not the case, however, with alkali molecules as may be seen by comparison of different figures in table VI above.

If we ascribe the regularity of constants among the molecules of the halogen group to the constancy of binding energy viz., 40 volts for this group, we are not yet able to account for the irregular variation among the alkalis though the binding energy is constant at 5 volts for them. The only source to which we can look for the elucidation of these facts is the expression for the binding energy, viz., the binding constant. This is given by

$$K = 2\pi^2 \omega_e^2 M \rho_e^2$$

where ω_e = nuclear frequency,

M = reduced mass of the molecule,

ρ_e = internuclear distance.

It gives the energy required to double the internuclear distance, if the harmonic law of force were valid over such distances. From the table of constants, we find that for the electronic states of the molecules under consideration, the nuclear distances are much larger for alkalis than for the halogen group. The maximum distance is 2.66 Å. in the case of halogens and nearly 4 Å. in the case of alkalis. It means that the harmonic law of force has to be valid over such ranges as 5.3 Å., in the case of halogens and about 8 Å., in the case of alkalis. As far as the halogens are concerned we can assume that for the

range 5.3 \AA° , the constancy of K explains to some extent a little of the regularity that is evident in table, but the same does not explain it in the case of alkalis for the range 8 \AA° . (which is in excess by 2.7 \AA° , over halogens), may be too large for the harmonic law of force to be valid. Further support can be lent to this contention by the values of the restoring forces which show some regularity in the case of halogens but not in the case of alkalis. If the law of harmonic force holds we can show that the restoring force which is the force required to increase the internuclear distance by one unit is given by

$$k = 4\pi^2 \omega_e^2 M$$

The values of k for the two groups are given below.

HALOGEN GROUP

Molecule.	No. of Electrons.	Restoring force k dynes/cm.
Cl-I	70	$2.374 \cdot 10^5$
Cl-Br	52	2.545 "
Cl-Cl	34	3.269 "
Br-I	88	2.065 "
Br-Br	70	2.452 "
Br-Cl	52	2.545 "
I-I	106	1.704 "
I-Br	88	2.065 "
I-Cl	70	2.374 "

ALKALI GROUP

Molecule.	No. of Electrons.	Restoring force k dynes/cm.
Li-Li	6	$.253 \cdot 10^5$
Li-K	22	.149 "
Na-Na	22	.017 "
Na-K	30	.013 "
K-K	38	.009 "
Li-Rb	40	.013 "
Li-Cs.	58	.0108 "
Na-Cs	66	.0105 "

SUMMARY

A simple empirical relation has been found to express roughly the nuclear frequencies of non-symmetric molecules in terms of those of symmetric molecules. This holds specially in the case of a group of analogous molecules like halogens and alkalies where for each group, the binding energy is roughly a constant. Other constants associated with these groups are also discussed in terms of the harmonic force law, the limitations of which have been pointed out.

Note added : After the above paper was submitted for publication, a communication by Howell appeared in 'Nature' (July 4, 1936) in which the author arrives at the same conclusions as those in the first part of the present paper with regard to the ground state vibrational frequencies of the alkali and halogen group of molecules.

CLUSTERING IN SIMPLE LIQUIDS

By

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(With 2 text figures.)

I. INTRODUCTION

While the author was engaged in the investigation of light-scattering in gases towards the close of 1931—to be exact in October of that year—he turned his attention to an examination of liquids by light-scattering method using incident horizontally polarised light. This arose out of a suggestion by Sir C. V. Raman (*Nature*, 128, 795, 1931) that atoms and molecules might act as Fitzgerald oscillators, in which case, by the method above mentioned, the horizontal component in the scattered radiation was expected to be much more intense than the vertical component.

It may be remarked here that carbon-tetrachloride was taken as the most favourable case wherein to look for $\Delta_{\parallel} > 1$ according to the then prevalent ideas,* since it is a symmetrical molecule with $\Delta_{\parallel} = 6\%$. A most exhaustive examination revealed no value greater than 1 for Δ_{\parallel} in C. Cl_4 .

This led to further systematic examination of liquids of diverse composition and families to see whether at least any other type gave a value for depolarisation greater than 1. A great variety of liquids were thus examined. Surprisingly enough, acetic acid showed this effect to a remarkable degree, persisting even after repeated distillation of the liquid in vacuo, several times. This effect was present in amyl alcohol and some few more liquids. This was quite unintelligible on any theory then known.

In 1934 Placzek published his valuable memoir in *Handbuch der Radiology* wherein he clearly pointed out that Δ_{\parallel} should in no case be greater than 1, neither for quadrupole radiation nor for magnetic dipole radiation.

But the publication recently of a paper by R. Gans in *Physikalische Zeitschrift* for 1936 (p. 20), has put the matter on a sound and

* All symbols are explained at the end of the paper.

understandable basis in the case of liquids. It is shown in that paper how scattering from clusters of molecules enhances the horizontal component, thereby giving a value for Δ_n greater than 1. Results obtained by the author in earlier investigations in 1931 are here recorded and a correlation made between them and the theory.

2. EXPERIMENTAL ARRANGEMENT AND RESULTS

The experimental arrangement followed is described below :

Sunlight was focussed by a lens L of 12 inches focus and 3 inches in diameter, immediately behind which was placed a big wooden screen S_1 with an aperture of $2\frac{1}{2}$ inches diameter to allow passage of light. F is a filter vessel containing alum solution to absorb the heat rays. The nicol N carries a disc marked in degrees around it and is placed with its electric vector horizontal. T is a tank containing

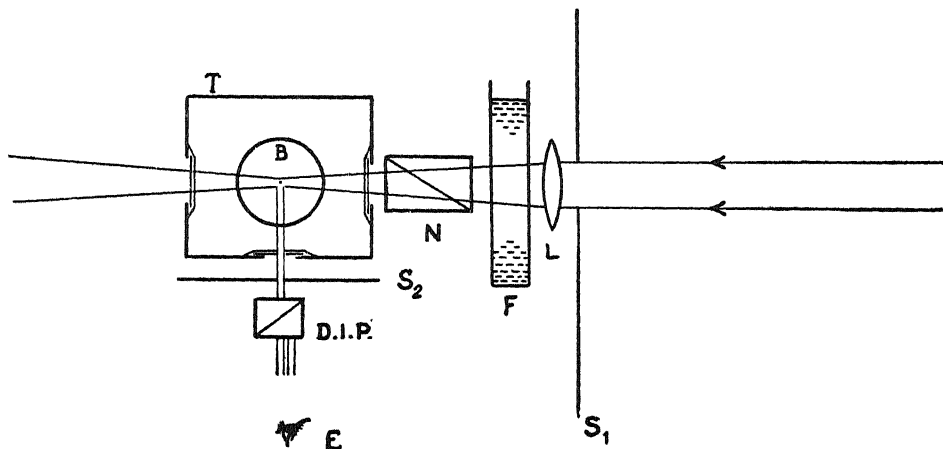


FIG 1

distilled water or a liquid of about the same refractive index as the liquid to be examined, and has three glass windows as shown in the figure. This is to set off any refraction effect of the spherical bulb B containing the liquid for examination. B contains the dust-free liquid, obtained after several distillations in vacuo, S_2 is another screen painted black on the side nearer to the observer, with a small aperture of 3mms square for observing the scattered beam. The double image prism D.I.P. is placed at a distance whereat the images are clearly separated. Whenever required, another nicol (N_2 , not shown), could be placed between the D.I.P. and the observer.

Observations on the nature of polarisation of the scattered light were made with only one nicol N and the double image prism. The

two images were seen as shown in Fig. 2, one above the other or side by side. A most delicate test to see whether both the images of the tract were equal in intensity or not, would be to rotate N_1 when, if they were equal, there would be only one position of equality; while for the other case, there would be found two positions of equality, separated by a small angle. This was the method adopted in all cases to decide immediately whether the horizontal

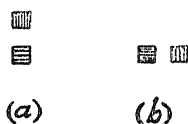


FIG. 2

component in the scattered track was more intense or not. If it were so, the angle through which N was rotated for getting the two tracks of equal intensity, was determined; and thereby the calculation made of the ratio of $\frac{H}{V}$. The other method of measuring this depolarisation by keeping N exactly with electric vector horizontal and rotating another nicol (N_2) placed behind D.I.P., was found to be unreliable, as it was found difficult to measure the ratio of intensities of two tracks differing very little from each other in intensity.

In cases where this anomalous polarisation was measured, it was only of a small magnitude, H being not more than 120% of V , in the most favourable case.

There is only one serious error which may vitiate the results, and that is the error arising from the convergence of the incident beam. For liquids with high values of Δ_u , Δ_v also is fairly high; and the lens used, if we consider it along with the aperture in the screen S , being $\frac{F}{4}$ the correction becomes important for $\Delta_v = 10\%$ and less. Accordingly, correction is made in all cases for the error due to the convergence of the incident beam.

The following table gives results of measurements of Δ_u made in distilled dust-free liquids. While qualitative observations were made in a great number of liquids—between fifty and sixty—measurements of exact depolarisation were made only in the following liquids.

Acetonitrile, benzonitrile and mesitylene were amongst those that were examined, but no appreciable difference in intensity could be noticed. This effect was most prominent in acetic acid, amyl alcohol and methyl alcohol. Formic acid was examined, but as it was found difficult to free it completely from dust, no measurements were made on it.

EXPERIMENTAL RESULTS

Liquids.	Δ_v %	Δ_h (experimental)	Δ_h (due to aperture of lens used)	Δ_h (corrected)
Acetic acid ...	30	1.18	1.014	1.16
Methyl alcohol ...	4.2	1.28	1.10	1.18
n-Propyl alcohol	3.9	1.19	1.10	1.09
Amyl alcohol (inactive)	6.4	1.15	1.06	1.09
Chloroform* ...	13.6	1.12(?)	1.03	1.09(?)
Benzene ...	30	1.00	1.01	1.00
n-Pentane ...	4	1.00	1.10	1.00
β -isoamylene ...	14.9	1.00	1.027	1.00
Carbon tetrachloride.	3.0	1.00	lenses of various apertures were used; result negative; always 1.00.	1.00

TABLE I

In the above Table, the first column gives the values of Δ_v as calculated from known values of Δ_u , the second column gives the experimentally determined values of Δ_h , the third column the values Δ_h would have for the aperture of the lens used, and the last column the values of Δ_h corrected due to convergence. It is seen that such correction for convergence is negligible for acetic acid, where the effect was found to be prominent.

It may be remarked here that no case was observed where Δ_h was less than 1. This is very significant.

3. DISCUSSION

Having established, beyond any experimental error, the genuineness of the value for Δ_h being greater than 1, it now becomes necessary to find an explanation for this anomalous polarisation.

*As chloroform undergoes photochemical decomposition on exposure to sunlight, Δ_h should not be taken too literally. That is why a query mark is placed against Δ_h .

The recent theory of R. Gans affords an explanation, but it remains to be seen how far it represents actual facts. We shall, however, proceed according to his theory.

Gans' theory takes account of scattering by clusters of molecules, in addition to the molecular scattering of light, and he derives three formulæ for three possible cases of clustering, namely (1) clusters in the liquid, of rod-shape, wherein the aggregation is said to occur end-to-end of molecules; (2) clusters of spherical shape; and (3) disc-like clusters. The ratio of $\frac{H}{V}$ is not the same for all the three cases. This ratio, when the incident light is polarised with electric vector horizontal, the electric vector being in the plane containing the incident and the scattered beams, is different for the above three cases, and they are given by,

$$\Delta_h = 1 - \frac{k^2 l^2}{14} \quad \dots \dots \dots (1)$$

$$\Delta_h = 1 \quad \dots \dots \dots (2)$$

$$\text{and } \Delta_h = 1 + \frac{k^2 \rho^2}{14} \quad \dots \dots \dots (3)$$

for the three cases respectively. Here

l is the length of the rod-like clusters,

ρ is the radius of the disc-like clusters

and $k = \frac{2\pi}{\lambda}$ where λ is the wave-length of light in the liquid.

It is, therefore, evident that since Δ_h is > 1 in all the cases, the clusters are all disc-shaped in the liquids examined in this paper.

Following Gans the radius of such disc-like clusters has been calculated for the liquids investigated and the results are given in the Table below.

TABLE II
RADIUS OF THE DISC-LIKE CLUSTERS

Liquids	Δ_h . (corrected)	Radius of the disc-like clusters in $\mu\mu$.
Acetic acid ...	1.16	95.0 $\mu\mu$
Methyl alcohol ...	1.18	101.0 "
n-Propyl alcohol ...	1.09	71.5 "
Amyl alcohol (inactive)	1.09	71.5 "
Benzene ...	1.0	—
n-Pentane ...	1.0	—
β -isoamyline ...	1.0	—
Carbon tetrachloride ...	1.0	—

The above results indicate clearly that only disc-like clusters were observed of radius between 70 to $100\mu\mu$ rather too large to ascribe them to molecular association. We know very well that in association, we meet with only aggregates of 2 or 3 molecules together, but never of the large size given here.

We must, therefore, postulate that this clustering is due to the thermal degeneration of crystal lattices, which are supposed to be present, but yet not in a well-ordered way as in crystals. In such cases, the clustering will be big, of the size of 100 molecules or more even, while generally there will be degeneration of larger aggregates. Such a hypothesis is not new, as X-ray diffraction in liquids lends support to this view. (See G. W. Stewart in *Physical Review* and in *Reviews of Modern Physics* for 1932).

It is really remarkable that we should meet with only disc-like clusters and not those of rod-shape. In the latter case, greater instability will result by a long chain of such molecules, about even 50 of them, and this is in accord with observation, as Δ_h was never found to be less than 1 even in a single case.

4. SUMMARY

With incident horizontally polarised light, scattering was observed in a number of liquids. Contrary to expectation, Δ_h was found to be >1 in some liquids. Considering these results in the light of Gans' theory, it is suggested that this higher value arises from the existence in such liquids of clusters of disc-shape. This affords an independent evidence for the view put forward by G. W. Stewart for the existence of "groups of molecules" in liquids, apart from associated molecules.

Bangalore, July 23, 1936.

Explanation of symbols used :

H indicates the horizontal component of the electric vector,

V indicates the vertical component of the electric vector,

Δ in general indicates the depolarisation factor, which is

$\frac{H}{V}$ (and not $\frac{\text{weaker component}}{\text{stronger component}}$);

The sub-letter for Δ indicates the nature of the incident light ; for example u , h and v standing for unpolarised, horizontally polarised and vertically polarised light respectively.

ON THE PHOTODISSOCIATION OF ALKYL HALIDES

PART II

By

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(With 4 Text figures)

I

The object of the present paper is to investigate the continuous absorption spectra of the Halogen Derivatives of Methane. The experimental part of the work has been reported in a previous paper by the author.¹ There has been a fair amount of work on the subject in recent years, most of which disagree in their experimental results.

The normal characteristic of the absorption spectrum of a molecule is the presence of bands. These bands converge to a definite limit, after which there is continuous absorption, indicating that one of the constituents of the molecule has gone out of the sphere of action of the other, in other words, dissociation has taken place. The energy of dissociation is given by the longwave limit of continuous absorption. These bands and continuous absorption are obtained as a result of an electronic transition between two discrete states of the molecule, both of which indicate stability. The excited (or upper) state is generally (though not always) of weaker stability. In some cases the upper state is highly unstable, so that, a transition to this state causes the molecule to dissociate with large amount of kinetic energy. The potential energy states of the molecules have been considered in detail by Finkelburg,² the author³ and others, to whose works reference may be made.

But the Alkyl Halides have got a characteristic type of absorption spectrum of their own, inasmuch as they show first a continuous absorption and then band absorption, as first reported by Herzberg and Scheibe⁴. According to Herzberg⁵ the whole pheno-

1. SEN-GUPTA, *Bull. Acad. Sc. U. P.* Vol. 2, p. 115, 1933.

2. FINKELBURG, *Phys. Zeits.*, Vol. 34, p. 529, 1933.

3. SEN-GUPTA, *Zeit. f. Phys.*, Vol. 88, p. 647, 1934.

4. HERZBERG and SCHEIBE, *Zeit. f. Phys. Chem.*, Abt. B. Vol. 7, p. 390 1930.

5. Herzberg, *Zeit. f. Phys.*, Vol. 61, p. 612, 1930

menon is connected with predissociation. It is well known that if there is a stable upper¹ state lying near about or overlapping an unstable (continuous) upper state, the latter influences the former to a marked extent, provided the transition of the molecule is not debarred by selection principles. Specially, when there is a crossing of the two upper curves, one stable and the other unstable, if the probability of transition to both of these from the ground level are nearly equal, loss of detail in the band structure corresponding to the point of intersection becomes evident. This is due to the fact that, at this point, the molecule may pass to the discrete state giving bands, as well as, to the continuous state giving continuous absorption; the two phenomena intermingle with each other.

The case of Methyl Halides is illustrated by Herzberg¹ in the following potential energy diagrams.

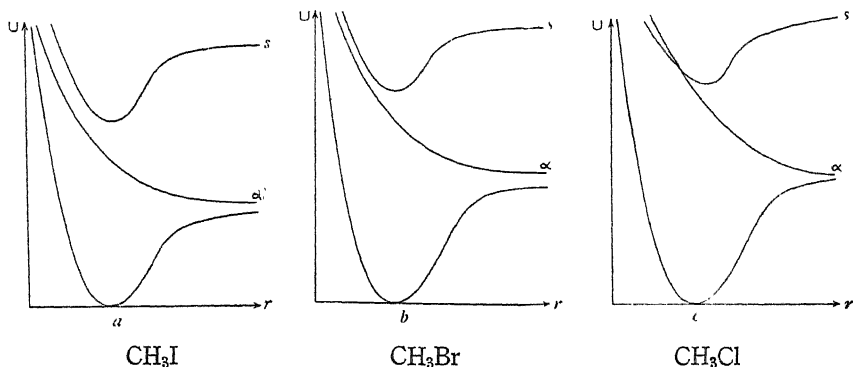


FIG. 1

Transition to the upper state (repulsive) gives a continuous absorption, and that to the stable upper state gives bands, the former obviously lying at longer wavelengths than the latter. The band system becomes more and more diffuse, as we proceed in the order CH_3I , CH_3Br , CH_3Cl , and moreover, the continuum overlaps the band system more. This is illustrated by the fact that the repulsive curve α approaches the stable curve s more and more, till in CH_3Cl we find them crossing each other. The bands in this case would be very diffuse near the point of intersection.

According to Mulliken,² the experimental behaviour of a compound like CH_3I can be explained by assuming for the normal state, the following,

1. HERZBERG, *loc. cit.*
2. MULLIKEN, *Phys. Rev.*, Vol. 47, p. 413, 1935.

$$(I s_c)^2 [s a_1]^2 (5 s_1 a_1)^2 [\pi e]^4 [\sigma a_1]^2 (5 p \pi_1 e)^4 \dots \dots {}^1A_1 \quad (1)$$

in which the orbitals $[s a_1]$, $[\pi e]$ etc. are given in the order of decreasing firmness of binding. But, of these the orbitals $5s_1$ and $5p\pi_1$ are non-binding, the latter having the least value. In the excited state, the $5p\pi_1$ electron, which is least firmly bound, passes to another orbital (αa_1) so that we get,

$$(\pi_I)^{-1} [\alpha a_1] \dots \dots \dots {}^{1,3} E. \dots \dots \dots (2)$$

We get several components in the transition ${}^1A_1 \rightarrow {}^{1,3} E$, though some of them may intermingle with each other on account of the continuous absorption. The two products of dissociation are CH_3 (2A) and I ($p^5 {}^2P_{3/2}$) or I ($p^5 {}^2P_{1/2}$) or both. The effect is similar in CH_3Br and CH_3Cl , in which the orbitals π_{Br} and π_{Cl} are affected. The absorption shifts towards shorter wavelengths because the ionisation potential of π_{Cl} is $>\pi_{Br} >\pi_I$.

II

In Table I the experimental results of different investigators have been given for the different compounds. The experiments of Herzberg and Scheibe (*loc. cit.*) and Henrici¹ were performed for the fluorite and quartz regions of spectra, while the others had been carried out mostly in the quartz region only. In CH_2I_2 , specially, three distinct absorption maxima have been obtained by Henrici, which are absent in the other compounds. It may be remarked here that the absence of absorption maxima in an experiment should not be always taken to indicate that they are really absent. Sometimes they are masked by other absorptions. In certain compounds like MoO_3 and TeO_3 , Dutta and the author² were able to obtain on plates, second and third maxima by control of pressure and temperature, though in a preliminary photograph there were no signs of them. The masking of subsequent maxima due to temperature has been dealt with by the author in a separate paper.³

1. HENRICI, *Zeit. f. Phys.*, Vol. 77, p. 35, 1932.

2. DUTTA and SEN-GUPTA, *Proc. Roy. Soc. A.*, Vol. 139, p. 397, 1933.

3. SEN-GUPTA, *Zeit. f. Phys.*, Vol. 88, p. 647, 1934.

TABLE I

Substance	1st Absorption		2nd Absorption	3rd Absorption
	Longwave beginning of continuous absorption λ Å	Maximum of continuous absorption, λ Å	Maximum, λ Å	Maximum λ Å
CH ₃ Cl	2200 (Sen-Gupta) ¹ 1900 (Herzberg and Scheibe) ³ 1995 (Henrici) ²	1725 (Henrici) ² 1744 (Herzberg and Scheibe) ³
CH ₂ Cl ₂	2500 (N. K. Saha) ⁴ 2090 (Henrici) ²
CHCl ₃	2600 (N. K. Saha) ⁴ 2126 (Henrici) ²
CCl ₄	2800 (N. K. Saha) ⁴ 2280 (Henrici) ²
CH ₃ Br	2325 (Herzberg and Scheibe) ³ 2415 (Henrici) ²	2000 (Herzberg and Scheibe) ³ 1943 (Henrici) ²
CH ₂ Br ₂	2507 "	1689 "
CHBr ₃	2863 "	1695 "
CBr ₄	3500 "	
CH ₃ I	2800 (Herzberg and Scheibe) ³ 3360 (Iredale and Mills) ⁵ 2952 (Henrici) ²	2550 (Herzberg and Scheibe) ³ 2550 (Iredale and Mills) ⁵ 2590 (Henrici) ²
CH ₂ I ₂	3342 "	3000 "	1973 (Henrici) ²	1868 (Henrici) ²
CHI ₃	1590 "

The longwave beginning of continuous absorption is of special importance, because it gives us the energy of dissociation (plus the kinetic energy of the dissociated partners). But this does not mean that if the absorption experiments are carried out at any arbitrary temperature, pressure or length of absorption column of the absorbing gas, the longwave beginning of continuous absorption would give the energy of dissociation of the molecule. This subject has been dealt

1. SEN-GUPTA, *Bull. Acad. Sc. U.P.*, Vol. 2, p. 115, 1933.
2. HENRICI, *loc. cit.*
3. HERZBERG and SCHEIBE, *loc. cit.*
4. N. K. SAHA, *Bull. Acad. Sc. U. P.*, Vol. 2, p. 239, 1933.
5. IREDALE and MILLS, *Proc. Roy. Soc. A.*, Vol. 133, p. 430, 1931.

with in several papers by different workers and the author. For obtaining a picture of the process a $U : r$ curve is generally useful with one stable ground state n , and one unstable upper state α . It is supposed that the molecule is residing in the o or lowest vibrational level A , and by the action of light passes to the state α , as shown by arrows in accordance with the Franck-Condon principle. According to Condon¹ the nature of the continuous absorption would be obtained as given by the curve BCD, that is, by reflecting the ψ function of the o -vibrational level from the curve α on the potential energy axis. The result is as shown. The absorption starts at an energy value given by B, becomes maximum at C, and ends at D. We see that the energy of dissociation is represented by AX , while the beginning of absorption gives a value AB for it. The maximum of absorption lies at C. The energy values given by the points B and C are higher than the actual value of the energy of dissociation given by the energy corresponding to the point X. From our absorption experiments, the least value of the heat of dissociation that we can obtain,

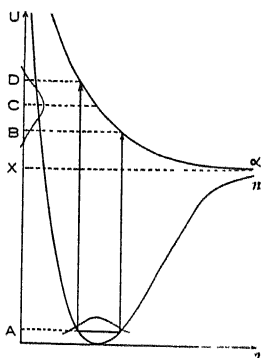


Fig. 2

is from the beginning (longwave) of continuous absorption. But this too is higher than the true value. The maximum of continuous absorption gives a still higher value. Hence we should not use the maximum of absorption for evaluating the energy of dissociation. To obtain this longwave beginning of continuous absorption, the experiments should be performed at the lowest temperature possible, to keep the molecule in the o -level. As the pressure or the column of absorbing gas is increased, the absorption shifts towards longer wave side, till a limit is reached when no further shift occurs. This limit is the true beginning of continuous absorption. As it is generally not possible to obtain this limit experimentally, the method employed by Herzberg and Scheibe (*loc. cit.*) and others, is to obtain several absorption spectra photographs at known increasing pressures. Then from the microphotometric records, a *percentage Intensity: pressure* curve is drawn for every wavelength. The intensity curve obeys the law

$I = I_0 e^{-\alpha p}$, in which α is the extinction coefficient. With the aid of the curves so obtained an $\alpha : \lambda$ curve is drawn, the point of intersection of which with the λ -axis gives the longwave beginning of continuous absorption.

1. CONDON, *Phys. Rev.*, Vol. 32, p. 858, 1928.

Apparently the same methods were used by different workers, but it is difficult to understand why the results for the same substance should be different, because there can be only one longwave limit if the molecule resides in the σ -level. Up to this time we have no evidence that increase of pressure raises the molecule to higher vibrational states.

III

From Table I, it is seen that the disagreement regarding the first longwave beginning of continuous absorption in the author's and Herzberg and Scheibe's (*loc. cit.*) results is rather glaring. (Some other pairs of results also show similar disagreement.) There is almost a difference of λ 300 Å in the two results. Moreover, from the respective photographs it appears that even the nature of continuous absorption of the author's photograph is quite different from that of Herzberg and Scheibe. The former is fairly and ends abruptly, while the latter is very much extended. It may be postulated that both these absorptions are simultaneously present, and, are due to two different processes of dissociation, though they could not be isolated in the same experiment. Such occurrences are not rare. A scrutiny of the Table I reveals, as Henrici and others have pointed out, that if we pass in the series CH_3Cl , CH_3Br , CH_3I or CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4 —that is, either substitute different halogens, or increase the number of the same halogen atom—the maxima (or longwave beginning) of absorption shifts more and more towards the longer wavelength side. This would indicate, as the different workers have pointed out, that the first continuous absorption represents the dissociation of a C-Halogen bond in every case.

In CH_3Cl , if we take the continuous absorption of Herzberg and Scheibe (or Henrici) as representing the breaking up of C-H bond, it might be suggested the author's limit of absorption at λ 2200 is due to the simultaneous breaking of a C-Cl bond in the molecule, so that the longwave limits of absorption in the two experiments would give the energies of the respective bonds. We see that the difference of bond energies of C-H and C-Cl bonds, as given by the two experimental limits is $143-130=13$ k. cal., while the calculated difference comes out as $123-107=16$ k. cal. (calculations given later)—a fairly good agreement for the type of experiment. We cannot get an exact value, as may be seen from the following considerations. In the first place, the energy of the C-H bond taken as 123 k. cal. has been calculated for CH_4 , so that it will have a slightly different value for CH_3Cl or other halogen substituted compounds. Secondly, when we break one of C-Cl bonds, the rest of the molecule, that is, (CH_3) , is in a highly

disturbed condition, so that the simultaneous or subsequent dissociation of a C-H bond may not require the same energy calculated for the normal state.

It is worth while testing this behaviour of the splitting of C-H and C-Cl bonds in the other compounds in the series CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4 . The calculated difference between the energies of the bonds C-H and C-Cl are given in Table II. The calculations have been discussed later.

TABLE II

Compound	CH_3Cl	CH_2Cl_2	CHCl_3	CCl_4
Difference in bond energy [(C-H) — (C-Cl)] in k. cal.	123—107=16	123 - 116.5 = 6.5	123 - 121.5 = 1.5	123 - 0 (no C-H bonds)

In CH_2Cl_2 , N. K. Saha (*loc. cit.*) could isolate from his extinction coefficient curves the two absorption processes due to the splitting of the C-H and C-Cl bonds. According to the present assumption he found that the experimental and calculated values of { (C-H) — (C-Cl) } agree remarkably. Saha's photogram did not show the two absorptions separately. In CHCl_3 he could not isolate the two absorption processes even from the extinction coefficient curves. This is just what we should expect, because from Table II we see that the value of { (C-H) — (C-Cl) } is too small. The very small value no doubt indicates, that the continuous absorption representing the splitting of C-H and C-Cl bonds almost overlap each other. We see, that, as more Cl atoms are substituted for H atoms, the absorption representing the breaking of C-Cl, at first distinct from that of C-H, approaches its value more and more till it merges almost into the other in CHCl_3 . In CCl_4 there are no C-H bonds at all, that is why no effect was obtained in the experiments. The behaviour of the Chloride group has to be verified for the Bromine and Iodine substituted compounds, but at present no data are available for these compounds. From the thermochemical calculations, however, we see that the energy differences { (C-H) — (C-Br) } and { (C-H) — (C-I) } are greater than that of { (C-H) — (C-Cl) }. Consequently, the two different continuous absorptions representing the splitting of C-H and C-Halogen bonds for Bromides and Iodides should be correspondingly more distinct than those of the Chlorides.

The results for the first longwave limit of continuous absorption for the compounds $\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_3\text{H}_7\text{Cl}$ and $\text{C}_4\text{H}_9\text{Cl}$ were found to be

almost the same as that for CH_3Cl by the author (*loc. cit.*). In these compounds we have to take into account the C-C bond also. Taking the value of the C-H bond energy as 123 k. cal., and that of C-Cl as 107 k. cal, (approximately, because the values cannot be exact), we get the energy of the C-C bond in each case, given in Table III. All

TABLE III

Compounds	$\text{C}_2\text{H}_5\text{Cl}$	$\text{C}_3\text{H}_7\text{Cl}$	$\text{C}_4\text{H}_9\text{Cl}$
Energy of the C - C bond in k. cal.	138.0	138.3	137.8

the values are in the near neighbourhood of 138 k. cal., corresponding to λ 2080 Å. This is so very near to the beginning of continuous absorption at λ 2200 Å (vide Table I) which represents the splitting of a C-Cl bond, that it is not surprising, that the process of absorption due to the breaking of a C-C bond could not be isolated from the others.

IV

For the explanation of the dissociation of a compound like CH_3Cl , Herzberg and Scheibe (*loc. cit.*) suppose that tetravalent C atom is in the ground state $s^2p^2 \rightarrow {}^3\text{P}$. The energies of the C-Halogen bond is given in the third column of Table IV, according to this assumption. Moreover, it was supposed by them, that when the C-Halogen bond breaks up, the dissociated halogens are in the excited metastable state ${}^2\text{P}_{3/2}$. It was not possible to test whether the other product of dissociation, for example, a Methyl group, were also excited or not, because the excitation states are still unknown at present. A scrutiny of the 2nd and 3rd columns of Table IV shows that the experimental values are too high—the discrepancy has been explained as due to the fact, that the products of dissociation have got a large amount of kinetic energy.

TABLE IV

Substance.	1st longwave limit of continuous absorption $h\nu$ in k. cal.	Energy of C-Halogen bond with C in ($s^2p^2\ ^3P$) state, in k. cal.	Energy of C-Halogen bond with C in ($sp^3\ ^3S$) state, in k. cal.	Energy of C-Halogen bond with C in ($p^1\ ^3P$) state, in k. cal.
CH_3Cl	130 (Sen-Gupta) 151 (Herzberg and Scheibe) 143 (Henrici)	78.0	107.0	128.2
CH_2Cl_2	114 (N. K. Saha) 137 (Henrici)	92.1	121.5	192.4
CHCl_3	110 (N. K. Saha) 135 (Henrici)	86.9	116.5	187.3
CCl_4	102 (N. K. Saha) 125 (Henrici)	81.6	111.4	182.1
CH_3Br	123 (Herzberg and Scheibe) 118 (Henrici)	67.1	96.1	117.3
CH_2Br_2	114 „
CHBr_3	100 „
CH_3I	102 (Herzberg and Scheibe) 85 (Iredale and Mills) 97 (Henrici)	43.5	72.5	93.7
CH_2I_2	86 „	50.0	79.5	150.4
CHI_3	179 (?) „	49.8	79.5	150.2

Some of the data used in the calculations are as follows :—

TABLE V

Heat of vaporization of C	161.0 (176.0) ¹ k. cal.
„ dissociation of Cl_2	58.0 k. cal.
„ „ „ Br_2	50.2 „
„ „ „ I_2	45.0 „
„ „ „ H_2	105.0 „

The method of calculation followed by Iredale and Mills and others are given below. The values in the third and fifth columns are new, while those in the fourth are Iredale and Mills' values recalculated with some later data by Saha or the author. The thermochemical

1. VAUGHAN and KISTIAKOWSKY, *Phys. Rev.*, Vol. 40, p. 457, 1932.

values used in the calculations have been taken from Landolt and Bornstein or International and Critical Tables.

Iredale and Mills have supposed that the tetravalent C atom is in the sp^3-^5S state.

1. Value of C (sp^3-^5S)—C ($s^2p^2-^3P$) = x :—

$$[C] = C(s^2p^2-^3P) - 161 \text{ (or 176)}$$

$$CO_2 = [C] + O_2 - 94$$

$$= \{C(^3P) - 161\} + [2O - 128] - 94$$

$$= C(^5S) - x - 161 - 128 - 94 + 2O$$

$$\text{i.e., } C(^5S) + 2O = CO_2 + 94 + 128 + 161 + x \dots \dots \dots (a)$$

$$\text{Again } CO = [C] + \frac{1}{2}O_2 - 26$$

$$= C(^3P) + O - 64 - 26 - 161$$

$$\therefore CO(^3P) + O = CO + 64 + 26 + 161 \dots \dots \dots (b)$$

Since (a) = (2.b)

$$x = 119 \text{ k. cal. (or } 134 \text{ k. cal, if}$$

$$[C] = C(^3P) = -176)$$

$$\text{i.e. } C(^3P) = C(^5S) - 119 \text{ k. cal.}$$

2. Value of C—H bond :—

Heat of combustion of Methane = 211 k. cal.

$$\text{i.e., } CH_4 + 2O_2 = CO_2 + 2H_2O + 211$$

$$= [C(^5S) - 119 - 161 - 94 + O_2]$$

$$+ (2H_2 + O_2 - 118) + 211$$

$$= [C(^5S) - 119 - 161 - 94 + O_2]$$

$$+ [4H - 210 + O_2 - 118] + 211$$

$$= C(^5S) - 491 + 4H + 2O_2$$

$$\therefore 1 \text{ C—H bond} = 491/4 = 123 \text{ k. cal.}$$

3. Value of C—I bond in CH_2I_2 :—

Heat of combustion of CH_2I_2 = 178 k.cal.

$$\text{i.e., } 2CH_2I_2 + 3O_2 = 2CO_2 + 2H_2O + 178 \times 2$$

$$= 2[C(^5S) - 119 - 161 - 94] + 2O_2$$

$$+ (4H - 210 + O_2 - 118) + 4I - 90 + 356$$

$$= C(^5S) + 3O_2 + 4H + 4I - 810$$

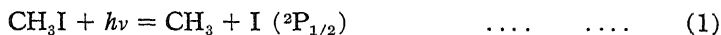
$$\therefore CH_2I_2 = C(^5S) + 2H + 2I - 405$$

$$\therefore 1 \text{ C—I bond} = \frac{405 - 2(123)}{2}$$

$$= 79.5 \text{ k. cal.}$$

V

From Table IV we see that if we suppose that the C atom in all these compounds is in the $s^2p^2\text{--}^3P$ state, the energy values of the C-Halogen bond are too low compared to the experimental results. As mentioned already, Herzberg and Scheibe assume that the process of photochemical dissociation is as follows,



so that, if we add the value of $^2P_{3/2}\text{--}^2P_{1/2}$ of halogen to the results given in column 3 of Table IV, there is still a large balance of energy, which is supposed to be the kinetic energy of the dissociated partners. Such a process would cause the upper repulsive curve in Fig. 1 to be unusually steep.

The values in column 4 of Table IV agree more nearly with the experimental results, but in some cases, contrary to experience, the theoretical value is higher than the experimental one.

Iredale and Mills too, suppose that the theoretical value of $h\nu$ is given by adding the value of $^2P_{3/2}\text{--}^2P_{1/2}$ of halogen to those given in column 4, according to the process (1) given above. Let us see how far this is possible. Taking CH_3I for example, the theoretical value of $h\nu = 75 + (^2P_{3/2}\text{--}^2P_{1/2})$ of I

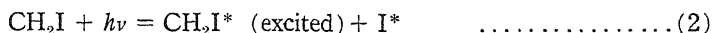
$$\begin{aligned} &= 75 + 22 \\ &= 97 \text{ k. cal.} \end{aligned}$$

The experimental value = 86 k. cal.

Such an assumption would be against all other experimental and theoretical evidences ; the theoretical value should be lower.

The calculations may be performed from a third point of view. Samuel and Lessheim¹ are of opinion, that, since there is no chemical or spectroscopic evidence of the difference in O atoms in CO_2 , the tetravalent C atom lies always in the $p^4\text{--}^3P$ state. They have evaluated the difference $\{\text{C } (p^4\text{ } ^3P)\text{--}\text{C } (s^2p^2\text{ } ^3P)\}$ as equal to 17.42 volts. The calculations based on this assumption are given in the last column of Table IV, but the results which agree very well with the experimental ones in CH_3Cl , CH_3Br , CH_3I , are too high for the others to be admissible.

There is no means of testing Henrici's (*loc. cit.*) postulate that second maximum in CH_2I_2 is due to a dissociation process as follows,



as they do not appear in the others at all. The absence of maxima is ascribed to the fact, that they become increasingly flatter and flatter and cannot be detected. This process is confirmed according to Henrici by the non-appearance of the maxima in CH_3I , CH_3Br , or CH_3Cl . But we may equally suppose, with Herzberg and Scheibe, that, in the latter case the dissociated (CH_3) radical may go to some higher excited states giving subsequent maxima. There are no data to test these postulates at present.

P. K. SEN GUPTA.

July 27, 1936.

* SAMUEL and LESSHEIM, *Curr. Sci.*, Vol. 2, p. 347, 1934.

CRITICAL OPALESCENCE OF CARBON-DI-OXIDE

By

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(With 3 text figures.)

1. INTRODUCTION

It is well-known that substances exhibit strong opalescence near the critical state. The Einstein¹-Smoluchowski² expression, based on the idea of a fluid as a continuous medium subjected to local changes of density, giving the fraction of light scattered by isotropic molecules in a transverse direction, is given by

$$I = \frac{2\pi^2 V}{\lambda^4 D^2} \cdot \frac{RT}{N} \cdot \frac{\mu^2 v \left(\frac{d\mu}{dv} \right)^2}{-dp} \cdot \sin^2 \theta.$$

where θ is the angle between the direction of observation and the electric force in the incident light, and where the other letters have the usual significance. This formula evidently gives enormous intensity near the critical state. In general, the molecules are anisotropic and the intensity given by them should also be considered. Ramanathan has worked out the complete theory; and taking into account the anisotropic nature of the molecule, he derives the following expression for the intensity of scattered light by a unit volume of the fluid;

$$I = \frac{I_0}{D^2} \left[\frac{\pi^2 RT \beta}{18 N \lambda^4} (\mu^2 - 1)^2 (\mu^2 + 2)^2 + \frac{\pi^2}{2 n_0 \lambda^4} (\mu^2 - 1)^2 r_1 \frac{(9 + 4\gamma)}{6 - 7r_1} \right]$$

where r_1 is the depolarisation of the scattered light, γ stands for $\frac{RT\beta}{N}$

$n_0 \left(\frac{\mu^2 + 2}{3} \right)^2$ and n_0 is the number of molecules per unit volume of the fluid. Raman and Ramanathan³ have investigated the validity of this formula over a series of pressures and find that the results are in better agreement with the second formula given above than with the first. It was with a view to testing the above formula near the

critical state with better experimental arrangement and with less uncertainties about temperature and background that this work was undertaken.

The physical properties of carbon-dioxide have been extensively studied, especially those of pressure-volume by Amagat, and the variation of refractive index with density by Phillips.⁴ Hence a complete study of the scattering at different pressures is made possible.

2. EXPERIMENTAL TECHNIQUE

The cross-tube used by Raman and Ramanathan in their investigations on CO_2 suffers from the defect, that the small windows being squeezed in, develop unequal strain, which therefore could not be used for polarisation measurements. Further, without suitable apertures inside, the walls themselves of the container vessel are likely to reflect the scattered light. A suitable cross-tube was therefore made.

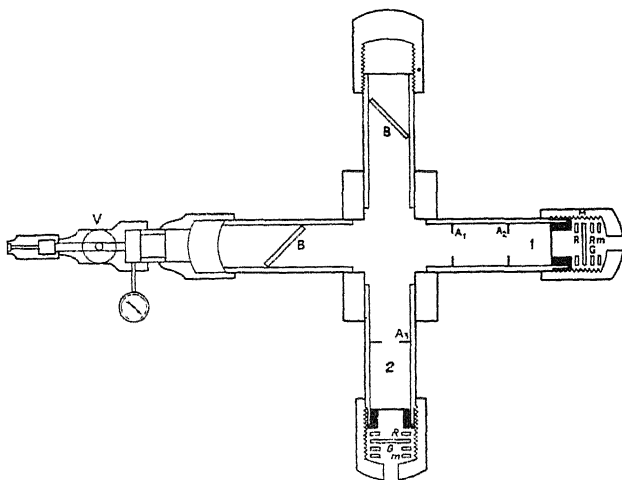


Fig. 1.

To the four sides of a hollow cube of iron are screwed in at 90° each, four cylindrical tubes of steel, as shown in figure 1. Steel arms 1 and 2 are meant for entrance of light and for making observations respectively and therefore carry glass windows of $\frac{1}{2}$ inch thickness, screwed in by suitable nuts. On either side of the glass window G, are placed rubber-washers R, and between R and the

cross-tube projects inside a dark cabin C through a hole made in the wooden wall. The other half of the beam enters a cylindrical glass tube with flat ends containing the standard liquid, with a similar system of suitable apertures. The latter glass tube is blackened fully except at ends for narrow regions, and in front for observation and is immersed in a tank of suitable refracting liquid. The light scattered by the liquid is viewed through a hole in the wall of the cabin, which admits only the arm of the cross-tube, screening off completely all extraneous light. The scattered light coming from the standard liquid and also from the cross-tube are at right angles and traverse equal distances before they enter the two faces of a Lummer-Brodhun cube L.B. and are viewed through a telescope T properly focussed. The observer sits inside the dark cabin for getting the eyes into a sensitive state and then views through the telescope the two beams side by side. The intensity of the standard which is usually more, is cut off by means of an Abney rotating sector photometer. The advantage in using the combination of both the rotating disc and the Lummer-Brodhun cube is to bring the two beams nearer for comparison when greater accuracy results.

The standard liquids employed were ether, benzene and carbon-di-sulphide, at various pressures of the gas in the cross-tube and finally the standards themselves were compared one against the other for computation.

The cross-tube was completely covered with cotton to prevent fluctuations in temperature and the room where these were arranged, was kept closed except for a small hole in the door for the entrance of the sunlight. This effectively prevented any draught of air entering in and kept the temperature fairly constant throughout.

3. INTENSITY AND POLARISATION OF SCATTERED LIGHT

Visual observations were made of the light scattered by CO_2 at various pressures and the following table gives the results of the intensity measurements. Column 4 gives the calculated values according to Ramanathan's formula corrected for the anisotropy of the molecule. Column 2 gives the ratio of the density of CO_2 at the pressure at which the intensity is observed to that at normal temperature and pressure. The last column gives the observed intensities in terms of that at one atmosphere pressure at 30°C .

TABLE I

Pressure in Atmospheres.	Density	Reciprocal of compressibility in atmospheres.	Intensity of density scatter- ing corrected for anisotropy.	Intensity of observed scattering.
	Density at N. T. P.			
20	20	18.7	29	26
30	32.1	23.0	59	59
40	47	29.4	77	78
45	54.5	30.4	112	117
50	64.5	31.5	144	142
55	75.7	30.2	207	208
60	89.7	27.9	315	312
65	109	22.9	576	572
68	127	19.1	940	962

The liquids, ether, benzene and carbon di-sulphide were also compared one against the other with the above arrangement of the rotating disc and Lummer-Brodhun cube and the ratios of intensities calculated accurately. These were taken at different stages in the above comparison.

Using the same cross-tube, the depolarisation of light scattered by CO_2 was observed at various pressures with a nicol and a double image prism in the track of the scattered light. The chief difficulty in the measurements of depolarisation is the photo-elastic effect of the window due to very high pressures, and the above cross-tube, at least to a great part overcomes the difficulty by so suitably screwing in the windows that the pressure on the windows is distributed uniformly. The following results show that at very high pressures, the observed values are systematically higher than the theoretical ones. However, we give the results below :

TABLE II

Pressure in atmospheres.	Depolarisation factor %	
	Observed.	Theoretical.
30	9.7	8
40	8.1	6
45	7.7	5.6
50	7.2	4.9
55	6.7	4.1
60	6.3	3.1
65	4.5	2

At low pressures and at pressures far removed from the critical state, where Boyle's law holds good, the depolarisation is given by

$$r = \frac{2f}{f+g}$$

while g has to be multiplied by γ , involving the compressibility of the gas, for all other pressures. For very large intensity the scattered light is very nearly polarised, just as it should happen near the critical state. For then,

$$g - \frac{4}{3}f = \frac{9}{16\pi^2 n_0^2} \left(\frac{\mu^2 - 1}{\mu^2 + 2} \right)^2$$

The above results indicate in a general way that the depolarisation is more complete as we approach the critical state, and the high values, higher than those indicated by the theory, have to be accounted for solely on the view, that the horizontal component in the scattered beam slightly increases in intensity owing to the formation of big aggregates of molecules. Such a state of aggregation can be expected just near the critical state, as just there, we are dealing with neither gas molecules, nor liquid molecules. A small increase in the horizontal component will not appreciably enhance the total intensity of scattered light, for the reason that the scattering is so enormous that it will remain pretty nearly constant. It may be observed that the intensities follow those predicted by theory.

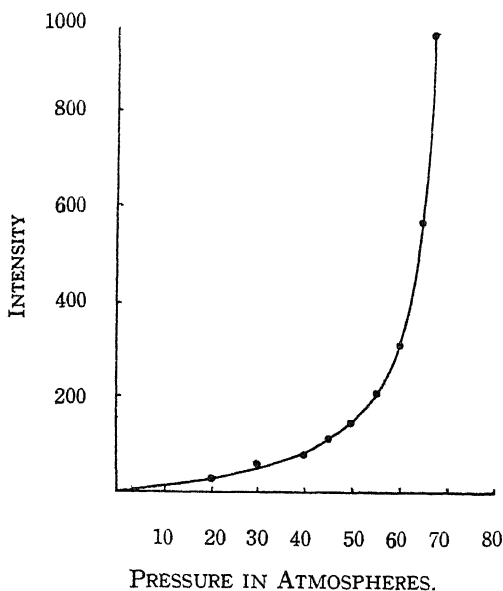


Fig. 3.

The accompanying graph (Fig. 3) shows the relation between the pressures and the intensity of scattered light. For very small changes in pressure beyond 60 atmospheres, the increase in intensity is enormous, so much so, what was only 312 at 60 atmospheres has gone up to 962, an increase of over three times, for an increase in pressure of only 8 atmospheres. The theoretical curve follows the one plotted in the figure closely, except that the points are displaced by very small units.

This work was completed at Calcutta about the beginning of 1933, and for various reasons could not be published earlier.

Bangalore, July 30, 1936.

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THE MEASUREMENT OF EFFECTIVE SOLAR ENERGY.

By

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INTRODUCTION

The need of an accurate knowledge of the solar energy is generally felt in medical science and profession. On account of the medicinal properties of ultraviolet light, there is always a demand for sources which give out such radiations in abundance. Apart from the artificial sources, such as, the mercury vapour lamp, emitting copious ultra-violet rays, there is the sun which is rich in radiations of different spectral characteristics. This is specially so for tropical countries like India, where the sun shines brightly for the greater part of the year. On account of both the beneficial as well as the injurious effects of ultraviolet light, the medical practitioner is always at an advantage, if he is in possession of an accurate knowledge of the effective ultraviolet energy to which we are subjected when exposed to the sun. A beginning has therefore been made to tackle this problem. A summary of quantitative results of this investigation has already been reported from this Laboratory in a paper (*Ind. J. Phys.* Vol. X, Pt. IV. 1936, p. 277). In the present communication we shall only deal with the details of the technique of measurement in all its aspects and the various calculations that are involved in the procedure, as the same could not be included in the previous communication for want of space.

EXPERIMENTAL.

The method used is that of spectral photometry. In any method of photographic photometry over large spectral ranges, it is necessary to take into account the variations due to plate sensitivity and wavelength. In the present problem, the range of the spectrum was from 3000 A.U. to 6400 A.U. In order to carry out the calibration over such a large wavelength range, it is necessary to possess a comparison standard which would give out continuous radiations covering the whole portion. A U.V. glass lamp taking a current of 1.9 amps with tungsten filament and sending radiations down to about 2700 A.U. was procured. This was calibrated in the usual way by means of Hilger's double monochromator in conjunction with a sensitive thermo-pile and a galvanometer. A curve of the lamp was prepared giving the relation of energy to wavelength ($E_{\lambda} : \lambda$) after applying due correction for dispersion of the monochromator and the absorption and reflection losses

in it. By using this energy curve, corrections for variation of intensity due to wavelength could be applied.

The actual procedure to measure the relative intensities in a given spectrum in terms of the standard chosen, is to obtain the photograph of the spectrum on a sensitive plate and put side by side blackening marks of known and graded intensities on it by exposure to the standard lamp. It should be remembered that uniform conditions must apply to both exposures. These refer to the time interval and the development. If they are satisfied, the blackening produced in any wavelength is a function of the intensity only. The standard lamp causes blackening on the plate due to a particular amount of energy radiated by it on the sensitive emulsion of the plate. The blackening being a measurable quantity, we could prepare at any wavelength in the spectrum of the standard lamp a curve which will relate intensity with the blackenings. At the same time the blackening produced by the given spectrum to be measured in the wavelength under consideration can be correlated to the intensity by means of the above curve. If, therefore, we chose several wavelengths at short intervals within the spectral region, we could get a blackening-intensity curve corresponding to each. This procedure gives, on a relative scale, the actual photographic intensities in different wavelengths of the spectrum. It does not, however, take into account any of the corrections such as the dispersion of the instrument or the varying plate sensitivity along the spectrum.

To apply the correction due to dispersion of the spectrograph we start with the energy curve ($E_\lambda : \lambda$) of the lamp. This energy of the lamp falling on the plate at any wavelength λ through the prism will produce a blackening proportional to $E_\lambda \cdot d\lambda$. It is with this energy that we are to compare the energy of the spectrum to be measured. Hence the curve $E_\lambda : \lambda$ is converted to $E_\lambda \cdot d\lambda : d\lambda$ by knowing the dispersion curve $d\lambda/dm : \lambda$ of the spectrographic instrument (dm being the same for different wavelengths). By reading the ordinates of this $E_\lambda \cdot d\lambda : \lambda$ curve, we can, by simple multiplication convert the photographic intensities to relative intensities in terms of the energy of the given lamp. This step incorporates the correction due to the plate sensitivity and the dispersion of the instrument.

It is interesting to see how our solar spectrum emerges after all these operations. The photograph of the solar spectrum was taken with a certain exposure resulting in a proportional amount of blackening. In order that the blackening of the solar spectrum at a particular wavelength should be determined, a definite scale of blackening should be established. This was done by using the principle that the intensity

of the light was proportional to the width of the slit. A step-slit consisting of five different widths was prepared. The widths were as follows :- 0.120, 0.255, 0.518, 0.974, 1.286 mm. Our known intensities are therefore in the above relation. Six photographs of the spectra of the standard lamp can be taken simultaneously with the help of this step-slit. At each wavelength the blackening in the different spectra will be proportional to the slit-widths, that is also

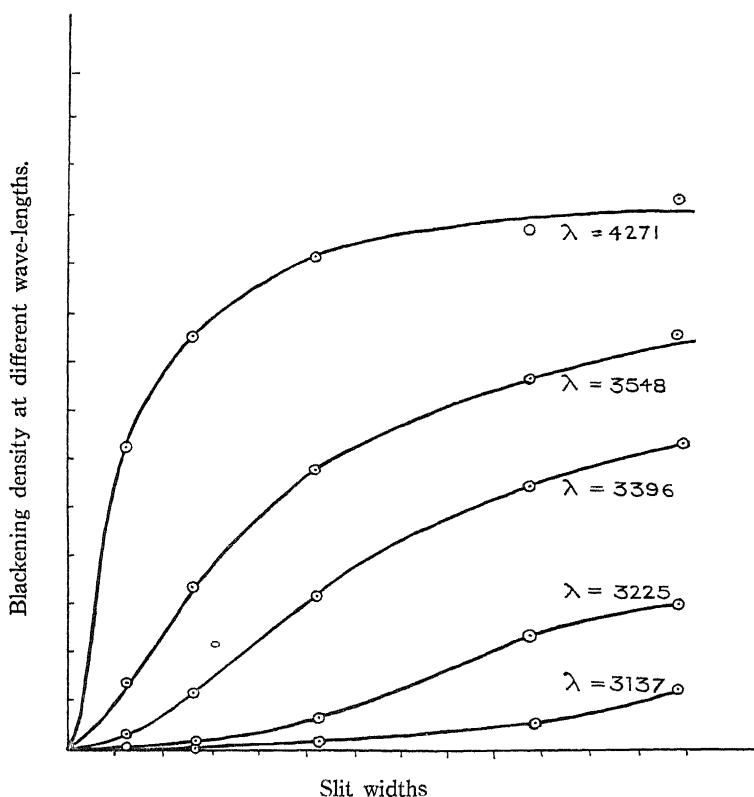


Fig. 1.

proportional to the intensities in the above ratio. If we call the blackening density of the spectrum taken with the widest slit as 100 and the blackening in the background of the unexposed part of the plate as 0, the blackening densities in corresponding wavelengths, of other spectral photographs taken with different slit-widths will be in proportion.

The relative blackening for any particular wavelength can be measured with a micro-photometer*, separately for all the five spec-

* The micro-photometer measurements were executed at Patna by the courtesy of the University Authorities.

tra, and a curve for that wavelength was prepared with slit-width i.e. intensity and blackening density as co-ordinates. Many such curves were prepared for a number of wavelengths at intervals of 30-50 Å units, some of these are given in fig. 1.

The blackening at different wavelengths of the solar spectrum was then measured with the micro-photometer and evaluated in terms of the intensity of the standard lamp with the aid of the numerous curves illustrated in fig. 1.

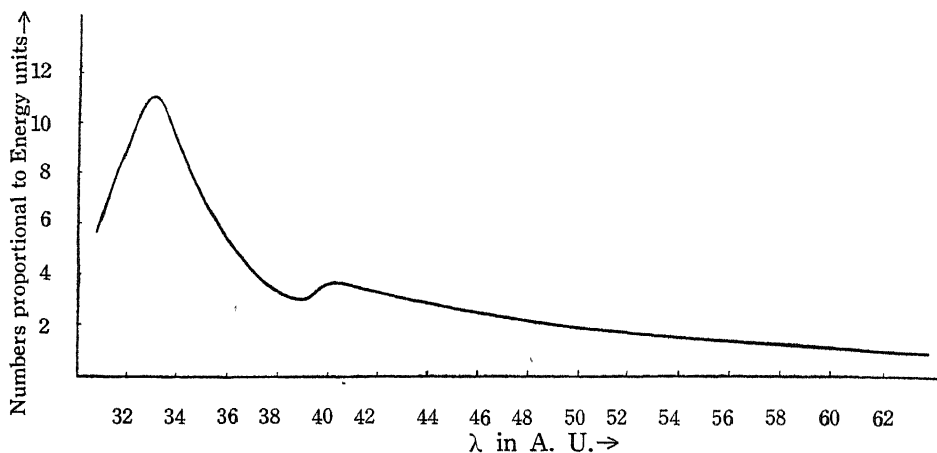


Fig. 2. The uncorrected energy curve of the solar spectrum.

The energy curve of the standard lamp as measured by the Hilger monochromator and modified after due corrections has been given below. (fig. 3.)

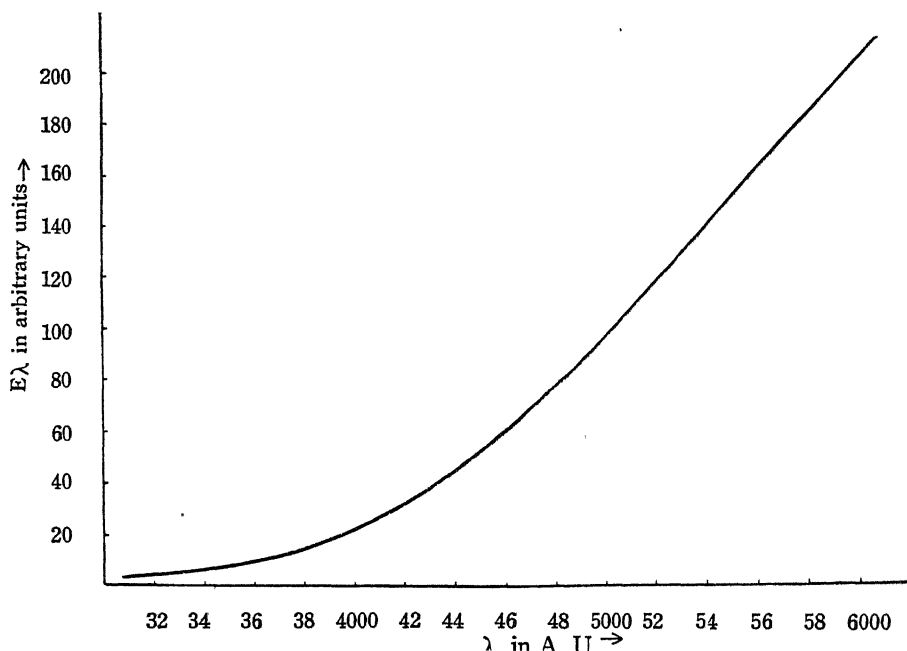


Fig. 4 below represents the dispersion curve $d\lambda/dm : \lambda$ of the spectrograph on which the measurements were made.

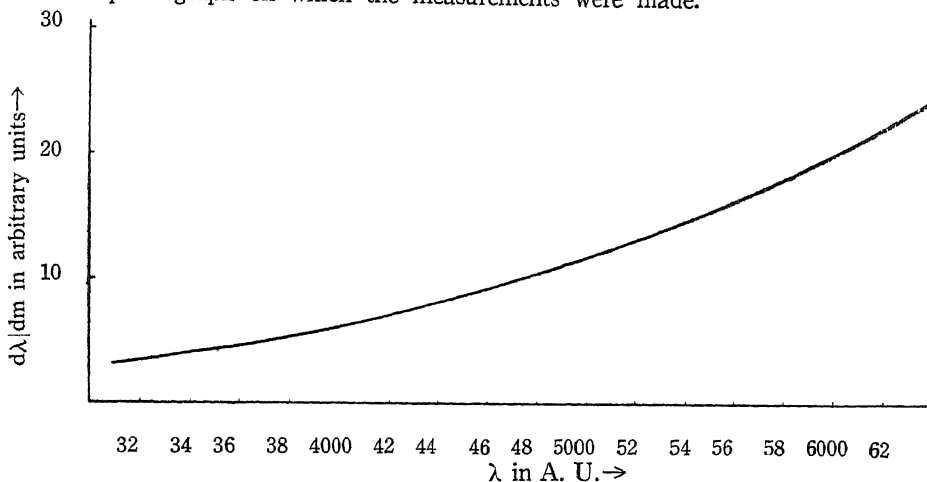


Fig. 4. Dispersion curve of the spectrograph.

The energy curve of the standard lamp as modified by the spectrograph is obtained by multiplying the ordinates of the curve in fig. 3 by those in fig. 4. The new curve $E_{\lambda} \cdot d\lambda : \lambda$ is given below in fig. 5.

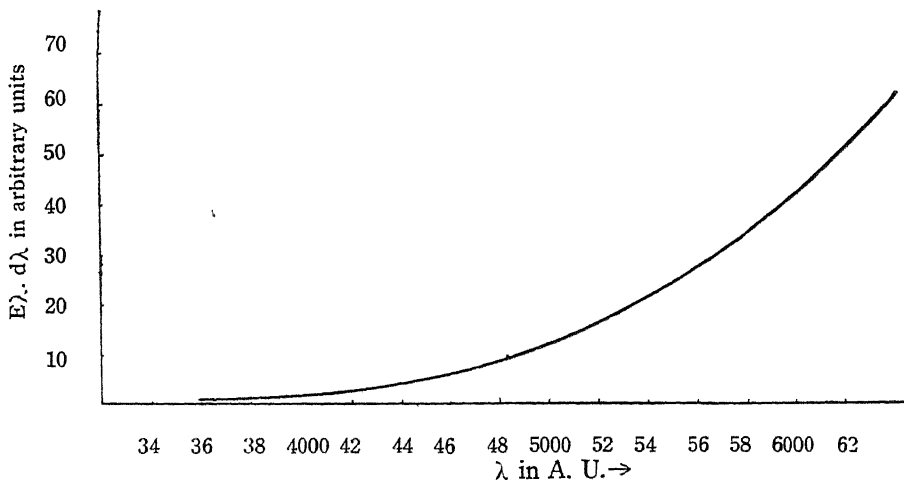


Fig. 5. $E_{\lambda} \cdot d\lambda : \lambda$ curve of standard lamp.

The above is therefore the final comparison curve representing the energy in terms of which we are to measure our solar spectrum at various wavelengths. In order to do this, we multiply the ordinates of fig. 1 by those of fig. 5 and thus construct a new curve representing the products at various wavelengths. The new curve

which is given below in fig. 6 gives the energy of the solar spectrum in terms of the standard.

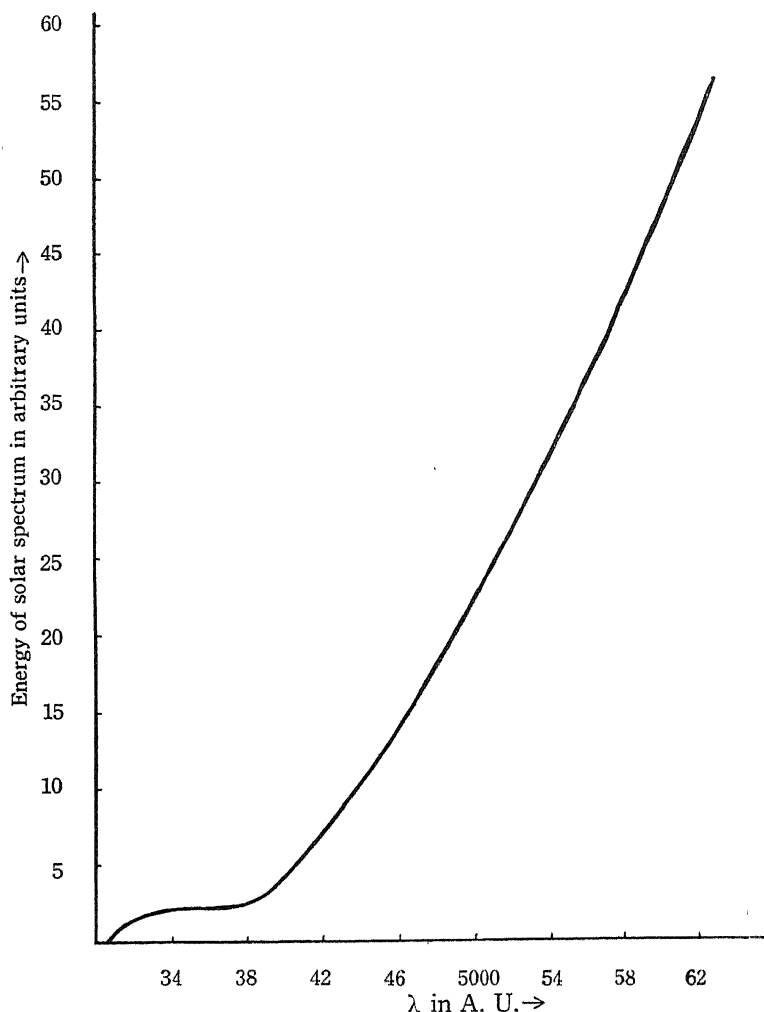


Fig. 6. The final corrected energy curve of the solar spectrum.

The areas under the respective portions of this curve above and below 4000 A.U. mark, represent the proportion of visible to ultra-violet energy of the sun approximately. These areas were accurately measured by a graphical method.

Conclusions : Thus it was revealed from these experiments that for every 100 units of the total visible and ultraviolet energy of the sun available in Bombay on a clear day in September, only 2.43 units are those of ultra-violet energy. Such a small percentage is probably due to strong absorption exerted by atmospheric ozone.

THE SCATTERING OF LIGHT BY A CLOUD OF WATER DROPS

By

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The theory of scattering of light by a sphere was first worked out by Lord Rayleigh¹ and has been successively developed by various workers for applications under particular conditions. The theory of Rayleigh is divided in three main parts, viz., (i) scattering by particles small in comparison with the wavelength of light, (ii) by particles comparable with the wave length of light, (iii) by particles considerably bigger in size.

Mie² has worked out in general outline a theory, which could be applied to particles of different sizes.

B. Ray³ investigated the scattering of light by fairly large particles and pushed forth the calculations to study theoretically the gradual changes of colour of the light transmitted through colloidal solutions and axial colours seen through drops of water.

Starting with Mie's formula Shoulejkin⁴ has treated the problem for different sizes of spherical dielectric particles and concluded that with gradual increase of size there is both reflection and refraction taking place. A definite asymmetry of scattering was noticed in case of particles having the size comparable to the wavelength of light.

The problem of intensity distribution at various angles by fairly large particles on the basis of Mie's theory has been a subject of Blumer's⁵ series of papers. He has plotted a number of curves of intensity distribution of the light scattered at various angles by particles of various sizes and of different refractive indices.

R. S. Krishnan⁶ has also applied Mie's formula to cases of particles of lower refractive index than the medium in which they are suspended.

Pokrowsky⁷ has modified the Rayleigh formula of scattering which he applied to practical investigations made by Dorno⁸ and later by himself.⁹

Webb¹⁰ has very recently obtained some results of scattering of light at various angles by fairly large drops of water, and water-alcohol mixture in air.

The present work was carried out with a view in the first place to apply Pokrowsky's relations to fairly large angles of scattering by a cloud of water drops of very large size as compared to the wave length of light. It is proposed to carry on the investigations to study the effect of the size of the drops and the wave length of light on the scattering in a particular direction, with special reference to the intensity of polarised and unpolarised light.

EXPERIMENTAL

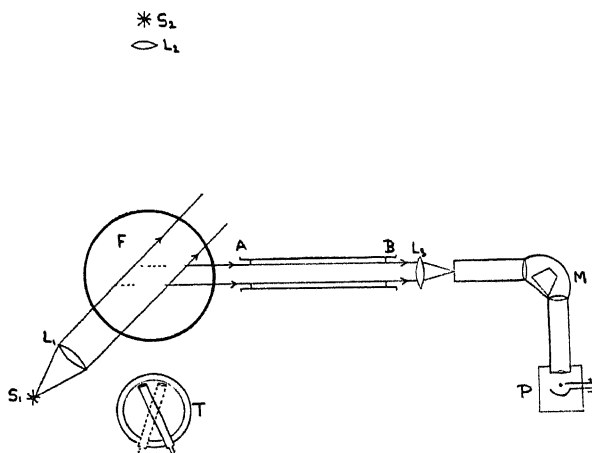


Fig. 1.

The actual experimental arrangement is shown in Fig. 1. The light from the source S_1 is focussed by the lens L_1 to a distant point so as to produce a fairly parallel beam of light. This beam passes through the flask F in which a cloud of water can be produced by sudden expansion. The rays of light scattered by the cloud of drops at any angle θ are allowed to pass through a tube AB of 30 cms. length and this beam is then focussed by the lens L_2 on the slit of the monochromator M ; the intensity of a particular wave length of scattered light can be observed by means of a photo-cell P . The size of the water drops in the cloud is observed by measuring the angular apertures of the dark diffraction rings formed by the monochromatic light from source S_2 passing through the cloud by means of a theodolite T . In order to change and measure the angle between the incident beam and the scattered beam, the light source S_1 and lens L_1 are mounted on the arm of a table similar to a spectrometer

so that they can together rotate about a vertical axis passing through the centre of the flask F. Thus it is possible to observe the scattering of light in any direction by keeping the tube T, lens L_2 , the monochromator M and the photo-cell P fixed and rotating only S_1 and L_1 .

In the particular results given below care was taken to produce clouds of uniform density and having same size of drops for any particular sets of measurements. This was done by controlling the expansion ratio and the number of nuclei on which the water condenses.

According to Rayleigh's theory, if a parallel beam of unpolarised light of intensity J_0 is scattered by a number of dielectric spheres, the intensity of scattered light J_θ in any direction making an angle θ with the incident beam is given by the following formula,

$$J_\theta = J_0 \times \frac{9\pi^2}{4\lambda^4} \times \left(\frac{\Delta\epsilon}{\epsilon}\right)^2 \times V^2 \times \left[\frac{I_{3/2}(z)}{Z^3}\right]^2 (1 + \cos^2\theta) N. \quad (I)$$

where

λ = wave length of light

ϵ = dielectric constant of the medium

$\Delta\epsilon$ = deviation of ϵ from the mean

V = volume of a scattering particle

$I_{3/2}(z)$ = the Bessel cylindrical function of order 3/2

N = number of scattering particles

$$Z = \frac{4\pi\rho}{\lambda} \times \sin \theta/2 \quad \dots \quad \dots \quad \dots \quad (II)$$

ρ = diameter of the particles

This relation can be used for spherical objects of constant density. In a general case, one must use a first approximation, as the actual detailed calculations are very long and tiresome. One can therefore take,

$$N = \frac{v_0}{V} \dots \dots \dots (III)$$

where v_0 = total volume of the scattering medium

$$\text{and } \frac{\Delta\epsilon}{\epsilon} = \frac{K}{\sqrt{V}} \dots \dots \dots (IV)$$

where K is a constant.

$$J_\theta = A v_0 (1 + \cos^2\theta) \phi(z) \dots \dots \dots (V)$$

$$\text{where } A = \frac{9 J_0 \pi^2 K^2}{4 \lambda^4} \dots \dots \dots (VI)$$

$$\text{and } \phi(z) = \frac{[I_{3/2}(z)]^2}{z^3} \dots \dots \dots (VII)$$

If we assume that the probability of light scattering for all values Z upto $Z_{(\max)}$ is the same corresponding to the relation (VII), then we get as the mean value

$$J_{\theta} = A v_0 (1 + \cos^2 \theta) \int_0^{Z_{(\max)}} \frac{\phi(z) dz}{Z_{(\max)}} \dots \text{(VIII)}$$

It has been shown by Pokrowsky that the value of this integral in (VIII) becomes constant for values of Z greater than 5. (In our case the values of Z are always greater than 8.) He has therefore expressed (VIII) in the following form by putting

$$\int_0^{Z_{(\max)}} \phi(z) dz = B = \text{constant} \dots \text{(IX)}$$

$$\therefore J_{\theta} = \frac{C_1 (1 + \cos^2 \theta)}{\sin \theta/2} \cdot v_0 \dots \text{(X)}$$

$$\text{where } C_1 = \frac{AB\lambda}{4\pi \rho_{(\max)}} \dots \text{(XI)}$$

If the scattered light is depolarised then the factor $(1 + \cos^2 \theta)$ must be considered as modified and for complete depolarisation

$$J_{\theta} = \frac{C_2}{\sin \theta/2}$$

It appears from (X) that for fairly large values of Z , i. e. $\frac{4\pi\rho}{\lambda} \cdot \sin \theta/2$ the intensity of scattered light will be proportional to $\left(\frac{1+\cos^2\theta}{\sin \theta/2} \cdot v_0\right)$ for different values of θ . Pokrowsky has shown the validity of this relation upto an angle of scattering of 5° only. In the present investigation, it has been possible to extend this result as far as 30° and for different wave lengths. It will be seen from Fig. 1 that the volume v_0 of the scattering medium will be more if the angle is small and less if the angle is large. v_0 will vary as $\frac{1}{\sin \theta}$ and consequently J_{θ} , the intensity will vary as $\frac{1+\cos^2\theta}{\sin \theta/2} \cdot \frac{1}{\sin \theta}$.

The results are tabulated below. The intensity of light is expressed as a factor proportional to the ratio of the intensity of scattered light and the direct unscattered light.

θ angle of scattered light	J_{θ} Intensity of the scattered light for wave lengths in A. U.			$\frac{1 + \cos^2 \theta}{\sin \theta/2} \cdot \frac{1}{\sin \theta}$
	6400	5800	5200	
7.5	30.20	18.00	...	232.8
8.0	10.80	203.9
10.0	17.40	11.10	8.50	130.2
12.5	13.50	8.20	7.30	82.9
15.0	7.40	6.10	5.70	57.2
17.5	6.60	5.10	4.90	41.7
20.0	5.00	4.30	3.80	31.7
25.0	4.30	2.70	2.60	19.9
30.0	1.40	13.5
ρ size of the drops in μ	5.90	5.90	5.80	

The results are plotted in fig. 2. It will be seen that a linear relation holds good for each of the wave lengths between the inten-

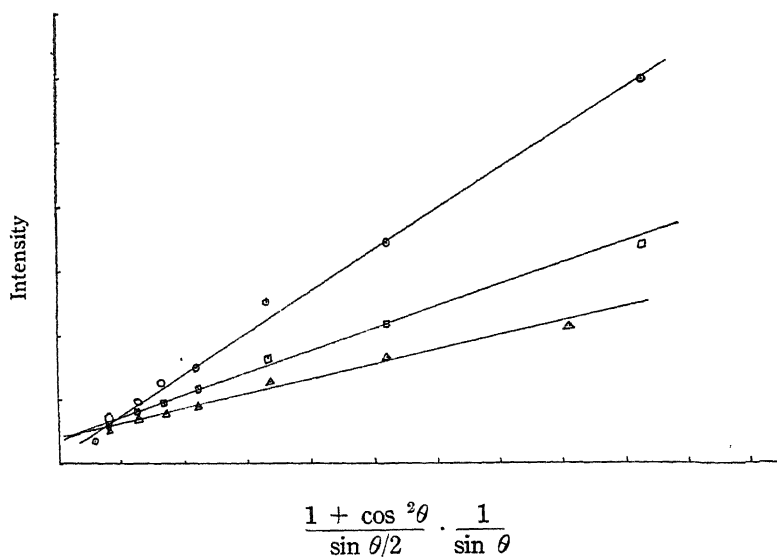


Fig. 2.

○ for 6400 A. U.
 □ for 5800 A. U.
 Δ for 5200 A. U.

size of drops 5.90 μ
 „ 5.90 μ
 „ 5.80 μ

sity of scattered light and the factor $\left\{ \frac{1 + \cos^2 \theta}{\sin \theta/2} \cdot \frac{1}{\sin \theta} \right\}$. It should be noted here that the smallest value of Z i.e. $\frac{4\pi\rho}{\lambda} \cdot \sin \theta/2$ is more than 8, and therefore the assumption that $\int_0^{z(\max)} \phi z dz = B =$ constant holds good.

It is evident from the graph that the intensity of scattered light for small values of θ , i. e., for large values of $\frac{1 + \cos^2 \theta}{\sin \theta/2} \cdot \frac{1}{\sin \theta}$, is more for larger wave lengths. This explains why the sky and the clouds round about the sun appear red at the time of sunset and sunrise.

For larger angles the smaller wave lengths seem to be scattered proportionately more.

The variation of the intensity of light with different wave lengths at a given angle can best be studied if the particle size of the cloud is the same for all wave lengths, because Z is a function of λ , ρ and θ simultaneously. Experiments in this direction are already in progress.

Thanks are due to Mr. P. B. Vaidya for his help in the experimental work.

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A DISCUSSION OF CONDUCTIVITY AND CATAPHORETIC
SPEED MEASUREMENTS OF COLLOIDAL PRUSSIAN
BLUE AND ARSENIOUS SULPHIDE FROM THE
POINT OF VIEW OF ORIGIN OF CHARGE ON
COLLOIDAL PARTICLES.

By

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According to the physical point of view the charge on colloidal particles is due to the adsorption of the ions of the peptising electrolytes on the surface of the particles (Mukherjee, *Koll. Zeit.*, 67, 178, 1934 and other papers by Mukherjee and co-workers ; Rabinovitch and Kargin, *Trans. Faraday Soc.*, 31, 50, 1935), while according to the chemical view the charge is due to the dissociation of the ionogenic complex attached to the surface of the colloidal particles (Pauli and Valko' *Electrochemie der Kolloide*—1929 ; Pauli, *Trans. Faraday Soc.*, 31, 11, 1935).

In previous papers published from our laboratory emphasis has been laid on the necessity of making simultaneous measurements of various properties of colloidal solutions under varying conditions, and it has been shown that the results can be easily understood by taking into consideration the changes in the preferential¹ adsorption by the colloid particles, of both the similarly and the oppositely charged ions as well as in the amount of electrolytes in the intermicellary liquid. In the present paper it is proposed to discuss some of the results of cataphoretic speed given in two of our previous papers (one by Mankodi, Barve and Desai and the other by Joshi, Barve and Desai, both in course of publication in the *Proc. Indian Acad. Sci.*²) and the simultaneous measurements of conductivity made at that time from the point of view of origin of charge on colloidal particles.

The conductivity was measured by the same method as that used by Desai and co-workers (*Indian J. of Physics*, 8, Part IV, 323, 1934).

1 The word "preferential" indicates that the ions are adsorbed in the inner sheet of the double layer.

2 Mankodi, Barve and Desai, *Proc. Indian Acad. Sci.*, 4 (4), 480, 1936 ; Joshi, Barve and Desai, *Ibid*, 4 (5), 1936.

RESULTS AND DISCUSSION

(a) *Changes in specific conductivity and cat. speed during dilution.*

In the following tables are given the cat. speed and specific conductivity on dilution of the prussian blue and arsenious sulphide sols dialysed for different periods.

TABLE I.

NOTE :—Readings in columns "a" and "b" refer to prussian blue sol dialysed for 3 days and 26 days respectively.

Dilution.	Cat. Speed $\times 10^5$		Sp. Conductivity $\times 10^6$	
	a	b	a	b
1	38.70	37.10	31630	270.9
2	42.50	32.30	16020	119.3
4	39.00	24.20	9194	72.8
8	30.10	21.50	4586	33.3

TABLE II.

NOTE :—Readings in columns "a" and "b" refer to arsenious sulphide sol undialysed and that dialysed for 31 days respectively.

Dilution.	Cat. Speed $\times 10^5$		Sp. Conductivity $\times 10^6$	
	a	b	a	b
1	50.65	21.40	226.3	212.0
2	33.60	24.80	115.5	105.8
4	21.70	29.00	51.7	45.5
8	17.40	41.20	28.9	30.4

The prussian blue sol dialysed for 3 days contained appreciable amounts of the peptising electrolyte (oxalic acid) as well as traces of ferric chloride, while that dialysed for 26 days contained only inappreciable amounts of the peptising electrolyte. Although the results with the sol dialysed for 26 days (Table I) would not seem to be against the chemical theory of the origin of charge, those with the one dialysed for 3 days cannot be reconciled with the same view, as although the sp. conductivity has decreased with dilution, the cat. speed

has first increased and then decreased. It has been shown in our previous paper (Mankodi, Barve and Desai, *loc. cit.*) that the changes in the cat. speed on dilution for both the short period and long period dialysed sols are due to changes in the amount of the active electrolyte in the sol which alter the distribution of the preferentially adsorbed ions on the surface of the particles. The changes in the sp. conductivity of the sol are mainly due to changes in the amount of the electrolyte contained in the intermicellary liquid and in the number of colloid particles per c.c., the influence of the size of the particles, the viscosity of the sol, the thickness of the double layer and the cat. speed being comparatively less marked (*Colloid and Capillary Chemistry* by Freundlich, Eng. Translation, 1926—p. 395).

In the case of the arsenious sulphide sol, (Table II) the sp. conductivity has decreased with increase of dilution for both the undialysed sol and the sol dialysed for 31 days. The undialysed sol did not initially contain any free arsenious acid, while the sol dialysed for 31 days contained some free arsenious acid as a result of hydrolysis of arsenious sulphide during dialysis (Joshi, Barve and Desai, *loc. cit.*). Arsenious sulphide may hydrolyse slightly during dilution. The changes in the sp. conductivity during dilution in the case of both the dialysed and undialysed sols are however considered to be mainly due to the changes in the number of colloid particles per c.c. of the sol.

The changes in the cat. speed on dilution of the undialysed arsenious sulphide sol (Table II) are probably mainly due to changes in the distribution of the preferentially adsorbed ions on the surface of the particles. In the case of the sol dialysed for 31 days the amount of free arsenious acid which is there in the sol, as a result of hydrolysis during dialysis, decreases on dilution; the increase in the cat. speed with dilution instead of decrease as in the case of the undialysed sol is probably mainly due to a decrease in the amount of arsenious acid (Joshi, Barve and Desai, *loc. cit.*). The chemical view point of Pauli and Valko' (*loc. cit.*) about the dissociation of the ionogenic complex on the surface of arsenious sulphide particles cannot explain satisfactorily the changes in sp. conductivity and cat. speed with dilution in the case of the sol dialysed for 31 days.

(b) *Changes in sp. conductivity and cat. speed during dialysis.*

The results of these experiments are given in Tables III & IV.

TABLE III.
Prussian blue sol.

Period of dialysis in days.	Cat. speed $\times 10^5$	Sp. Conductivity $\times 10^6$
3	38.70	31630.0
8	40.60	8780.0
13	43.20	2156.0
17	42.50	1116.0
21	41.05	554.4
26	37.10	270.9

TABLE IV.
Arsenious sulphide sol.

Period of dialysis in days.	Cat. speed $\times 10^5$	Sp. Conductivity $\times 10^6$
0	50.65	226.3
4	34.15	181.1
8	26.10	167.0
17	39.25	284.5
23	45.70	213.1
29	36.00	209.6

From Table III it will appear that with the progress of dialysis of prussian blue sol the sp. conductivity decreases as during dilution. The decrease in the sp. conductivity with the progress of dialysis is mainly due to a decrease in the amount of the peptising electrolyte and in the number of particles per c.c. because the turbidity of the sol increases during dialysis. The changes in the cat. speed during dialysis are, as stated in our previous paper (*loc. cit.*), due to changes in the amount of the peptising electrolyte which alter the distribution of the preferentially adsorbed ions on the surface of the particles. It is thus not possible to account for the variations in the cat. speed as arising out of changes in the ionic strength as assumed by Pauli and Valko' (*loc. cit.*).

The changes in the sp. conductivity with the progress of dialysis of arsenious sulphide sol are very interesting (Table IV). It will appear that the sp. conductivity first decreases and reaches a minimum, then increases and reaches a maximum after which it again decreases on carrying the dialysis to extreme. As stated above this sol initially

did not contain any free arsenious acid. With the progress of dialysis however, arsenious sulphide hydrolyses and the amount of free arsenious acid in the sol increases upto a dialysis of 8 days, decreases between 8 and 14 days and remains constant thereafter (Joshi, Barve and Desai, *loc. cit.*). One would ordinarily expect that the sp. conductivity with the progress of dialysis of arsenious sulphide should first increase and then decrease and remain practically constant thereafter if the changes in the amount of free arsenious acid in the sol during dialysis were controlling it. The changes in the sp. conductivity of this sol with dialysis are therefore due to some other factors. As a result of hydrolysis the number of particles of arsenious sulphide per c.c. will decrease but the number of particles of colloidal sulphur, produced as a result of oxidation of H_2S , will increase at the same time. It is likely that the decrease in the sp. conductivity in the early stages and later stages of dialysis might have mainly been due to a greater rate of decrease of the number of arsenious sulphide particles than of increase in the number of sulphur particles. The intermediate increase in the sp. conductivity (Table IV) is perhaps due to the fact that as a result of decrease in the amount of free arsenious acid, the peptisation of the sol takes place, thus giving rise to a greater number of particles per c.c. It should be mentioned that the above explanations of changes in the sp. conductivity of arsenious sulphide during dialysis are only tentative and some other causes might also be responsible for these peculiar changes. These points are being investigated. The changes in the cat. speed during dialysis have been explained in our previous paper (*loc. cit.*) as being due to changes in the amount of electrolytes in the sol, resulting in a change in the distribution of the preferentially adsorbed ions on the surface of the particles.

(c) *Changes in sp. conductivity and cat. speed during ageing.*

TABLE V.
Prussian blue sol dialysed for 25 days.

Age in days.	Cat. speed $\times 10^5$	Sp. Conductivity $\times 10^6$
0	38.60	65.3
20	38.30	63.6
38	31.55	41.9
104	27.90	34.2
173	27.40	33.4
218	27.20	32.7

TABLE VI.
Arsenious sulphide sol.

Age in days.	Cat. speed $\times 10^5$	Sp. Conductivity $\times 10^6$
0	37.05	145.0
15	34.95	160.3
30	29.35	196.1
45	20.50	236.2
60	18.15	191.9
90	16.30	114.8

It will appear from Table V that the changes in both the sp. conductivity and cat. speed of prussian blue are more marked during the first thirty days than afterwards. The changes in the sp. conductivity in the beginning may be mainly due to a preferential adsorption of the oppositely charged ions from the intermicellary liquid which possibly gives rise to a slight increase in the size of the particles, thus decreasing their number per c.c. at the same time. The decrease in the cat. speed is also probably due to a preferential adsorption of the oppositely charged ions from the intermicellary liquid.

In the case of arsenious sulphide sol (Table VI), the changes in the sp. conductivity and cat. speed on ageing are not in the same direction for the first 45 days. The amount of arsenious acid in the sol increases with age (Joshi, Barve and Desai, *loc. cit.*) and the initial rise in sp. conductivity might be probably mainly due to this increase in the amount of free arsenious acid. The decrease of sp. conductivity after 45 days in spite of an increase in the amount of free arsenious acid suggests that some other influences are also at work. As a result of increase in the amount of free arsenious acid in the sol, the preferential adsorption of the oppositely charged ions will increase resulting in an increase in the size of the particles and consequently a decrease in their number per c.c. Freundlich (*Zeit. f. Physik. Chemie*, 80, 566, 1912; also see Krestinskaya, *Koll. Z.* 66, 58, 1934) has emphasised the coarsening of the particles in the arsenious sulphide sol on ageing (cf. R. S. Krishnan, *Proc. Indian Acad. Sci.* 1, 44 & 211, 1934; 717, 1935). It thus appears that after 45 days, the influence of the decrease in the number of particles per c.c. on the sp. conductivity becomes so marked that the increase in the same which results due to an increase in the amount of arsenious acid is not allowed to be noticed at all. The decrease in the cat. speed on ageing is due

to an increase in the preferential adsorption of the oppositely charged ions on account of an increase in the amount of arsenious acid in the sol. It must be mentioned here that the chemical theory of the origin of charge (Pauli and Valko', *loc. cit.*) cannot explain the simultaneous changes observed by us in the sp. conductivity and cat. speed on ageing of the sol.

(d) *Changes in sp. conductivity and cat. speed on exposure to sunlight.*

The results of experiments are given in Tables VII & VIII.

TABLE VII.
Prussian blue sol dialysed for 21 days.

Exposure to sunlight in hours.	Cat. speed $\times 10^5$	Sp. Conductivity $\times 10^6$
0	42.70	154.5
1	37.80	27.2
2	36.20	31.4
5	34.10	33.0
10	33.60	41.3
29	27.60	127.1

TABLE VIII.
Arsenious sulphide sol.

NOTE :—Readings in columns "a" and "b" refer to arsenious sulphide sol undialysed and that dialysed for 35 days respectively.

Exposure to sunlight in minutes.	Cat. speed $\times 10^5$		Sp. conductivity $\times 10^6$	
	a	b	a	b
0	50.10	36.20	259.2	425.9
30	51.25	...	281.5	...
60	...	30.05	...	653.1
70	48.35	...	287.8	...
150	43.80	...	359.8	...
300	34.05	17.40	754.8	1434.0
450	32.05	...	1128.0	...
600	...	14.25	...	1825.0
1200	29.85	...	1920.0	...

The changes in the sp. conductivity and cat. speed on exposing the prussian blue sol to sunlight are not in the same direction except for the first one hour (Table VII). The changes in the cat. speed on exposure are probably due to action of sunlight on oxalic acid which gives rise to a change in its amount in the intermicellary liquid and in the distribution of preferentially adsorbed ions on the surface of the particles. The initial decrease in the sp. conductivity is probably due to the fact that agglomeration of the particles results, giving rise to a decrease in their number per c.c. The subsequent increase in the sp. conductivity is perhaps due to desorption of the preferentially adsorbed similarly and oppositely charged ions, thus increasing the amount of free electrolyte in the intermicellary liquid. Small changes in the cat. speed after 1 hour's exposure, in spite of a marked increase in sp. conductivity, suggest that almost an equal amount of similarly and oppositely charged ions is desorbed thus keeping the excess of the preferentially adsorbed similarly charged ions to the preferentially adsorbed oppositely charged ions about the same.

In the case of the undialysed arsenious sulphide sol (Table VIII) as well as the sample dialysed for 35 days the sp. conductivity has continuously increased while the cat. speed decreased at the same time except for the former sol on short exposures when the cat. speed has actually somewhat increased. It has been found that the amount of free arsenious acid in the sol continuously increases on exposing it to sunlight (Joshi, Barve & Desai, *loc. cit.*). On exposure the size of the particles increases and their number per c.c. decreases and the specific conductivity should have decreased due to this effect. The continuous increase in sp. conductivity in spite of this is probably due to the fact that the influence of the increase in the amount of free arsenious acid in the sol is so marked that the decrease due to aggregation of particles is not allowed to be noticed at all. The initial increase in the cat. speed for the undialysed sol which does not contain any free arsenious acid in the beginning, is due to production of free arsenious acid in the sol which increases the preferential adsorption of the similarly charged ions.

The sol dialysed for 35 days already contained appreciable amount of free arsenious acid from the beginning and hence production of further arsenious acid on exposure to light did not show an initial increase in the cat. speed. The decrease in the cat. speed is due to an increase in the preferential adsorption of the oppositely charged ions due to a continuous increase in the amount of free arsenious acid in the sol.

SUMMARY AND CONCLUSIONS.

From a discussion of results of simultaneous measurements of specific conductivity and cataphoretic speed of colloidal prussian blue and arsenious sulphide during dilution, dialysis, ageing and exposure to sunlight, it is shown that the changes in conductivity and cat. speed can be easily understood if it is assumed that the charge on the particles is due to preferential adsorption of the ions of the electrolytes present in the sol. The chemical view point about the origin of charge which is based on the dissociation of the ionogenic complex on the surface of the particles is not supported by our results.

Received 15th April, 1936.

DIARYL-p-NITROBENZAMIDINES

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In course of his previous work, the author found that diphenyl-p-aminobenzamidine mono-hydrochloride exhibited the phenomenon of chromoisomerism, it being obtainable in two forms, one colourless and the other yellow (*J. Ind. Inst. Sc.*, 1924, 7, 205). As chromoisomerism had not been previously met with in amidines, a further study of the phenomenon appeared desirable. To ascertain whether the phenomenon was an isolated case or was of a more general nature, some diaryl-p-nitrobenzamidines have been synthesised for examination from this point of view.

This paper describes the synthesis of diphenyl, phenyl-p-tolyl-, and di-p-tolyl-p-nitrobenzamidines, which were prepared from the appropriate anilide-imido-chlorides.

The following observations of interest have been made during the course of the work :—

1. The product of the action of phosphorous pentachloride on p-nitrobenz-p-toluidide is the imido-chloride, and not the amido-dichloride as stated by Gattermann and Neuberg (*Ber.* 1892, 25, 1081). These authors give the melting point of their so called amido-dichloride as 119°, which is very near the melting point of the imido-chloride obtained by the author, viz., 120°. Gattermann and Neuberg removed phosphorous oxychloride by heating the reaction product at 100-110° in vacuum and crystallised the crude product from ether. In the present work, the product was isolated under milder conditions by pouring the reaction product into petroleum ether, when the imido-chloride was precipitated in the crystalline condition, the phosphorous oxychloride remaining in solution. The amido-dichloride, if at all present, had thus the greater chance of being isolated in the author's experiments than in those of Gattermann and Neuberg. The well-known instability of amido-dichlorides further makes the assumption of the product being an amido-dichloride highly improbable. p-Nitrobenzanilide also gives the imido-chloride (Shah and Chaubal, *J.*, 1932, 651).

2. Phenyl-p-tolyl-, and di-p-tolyl-, p-nitro-benzamidines are found to be red and orange compounds of m.p.s. 138° and 160° respectively. These substances are said by Gattermann and Neuberg (*loc. cit.*) to have been prepared by the action of aniline and p-toluidine on their supposed amido-chloride, and are described as colourless and sparingly soluble substances of m.p.s. 260° and 300° respectively. It is obvious from their method of working that the substances described by them as the free nitrobenzamidines are the hydrochlorides.

3. The compound obtained by condensing p-nitrobenzanilide-imido-chloride with p-toluidine is identical with that obtained by condensing p-nitrobenz-p-toluidide-imido-chloride with aniline. This is in accordance with the established tautomeric character of amidines.

4. Diphenyl-p-nitrobenzamide possesses the property of entering into combination with the majority of solvents. The composition of the resulting compounds in the five cases investigated, is two molecules of the benzamide to one molecule of the solvent. These compounds differ in colour and in stability according to the solvent, that with pyridine being the least stable, and breaking down into its components at the ordinary temperature in a few hours. The phenyl-p-tolyl- and di-p-tolyl-compounds show the same property in a lesser degree. This property is lost in the acetyl and benzoyl derivatives.

5. The nitrobenzamidines and some of their salts show the phenomenon of either chromoisomerism or thermotropy. This will be dealt with in a subsequent communication.

EXPERIMENTAL

p-Nitrobenzanilide.—Only a poor yield of p-nitrobenzanilide could be obtained by heating together p-nitrobenzoic acid and aniline, with or without the addition of PCl_3 . It was therefore prepared from p-nitrobenzoyl chloride (22 g.) which was gradually added to a mixture of aniline (12 g.) and diethylaniline (23 g.) with occasional cooling; the mixture was finally heated for half an hour on the water bath. The cold mass was ground up with dilute HCl and after filtration and washing with dilute NaOH and water, was crystallised from glacial acetic acid in colourless flat needles (24 g.) of m.p. 216° . (*Beilstein*, XII, p. 268—m.p. 204° , 210 – 211° ; Brady and Mehta, *J. C. S.* 1925, 125, 2301—m.p. 214°).

p-Nitrobenzanilide-imido chloride was prepared from the above anilide by the action of phosphorous pentachloride (Shah and Chaubal, *loc. cit.*).

Diphenyl-p-nitrobenzamidine.—It has been prepared before (probably in a very impure condition) by heating together the condensation product of p-nitrobenzyl cyanide, and nitroso diethylaniline, with aniline hydrochloride in alcoholic solution. It is described as an uncrystallisable powder (no m.p. given) very soluble in all solvents (Sachs and Bry, *Ber.*, 1931, 34, 118).

It was prepared in the present instance from the above imido-chloride by the author's method (*loc. cit.*) by condensation with aniline in presence of diethyl-aniline. The imidochloride (20 g.) was ground up with diethylaniline (15 g.) and aniline (7 g.) added in small portions, cooling at intervals. The reaction mixture, which soon set to a solid mass, was heated on the water bath for half an hour. Dilute HCl was added to dissolve the diethyl aniline and excess of aniline. The solid residue, of the nitroamidine hydrochloride, after filtration and washing with water was dissolved in boiling alcohol, with the addition of a little strong ammonia to liberate the amidine. The clear solution deposited on cooling orange coloured plates which were recrystallised from hot benzene. These crystals contained benzene of crystallisation on removal of which by heating at 100-110° for 4 hours, the compound was obtained as a yellow powder m.p. 155°. It is easily soluble in hot alcohol, benzene, carbon-tetrachloride and petroleum ether, and sparingly soluble in cold. It dissolves easily in acetone, chloroform and pyridine (Found : N, 13·4 ; $C_{19}H_{15}O_2N_3$ requires N, 13·2 per cent.).

Solvent of crystallisation.—It was observed that the crystals from various solvents when left for some time or more quickly when heated became opaque, changed colour, and in some cases crumbled to a yellow powder. This change is due to loss of solvent of crystallisation. The substance was crystallised from various solvents and the crystals obtained from different solvents examined with the following results:—

Solvent.	Colour.	% loss of weight on heating at 110° at 100 m.m.	
Benzene	Orange	10·7	$2C_{19}H_{15}O_2N_3$, C_6H_6 requires loss, 10·9 per cent.
Carbon-tetra-chloride	Deep Orange	20·6	$2C_{19}H_{15}O_2N_3$, CCl_4 requires loss, 19·5 per cent.

Solvent.	Colour.	% loss of weight on heating at 110° at 100 m. m.	
Ethyl-alcohol	Yellowish Orange	6.6	$2C_{19}H_{15}O_2N_3$, C_2H_5 O H requires loss, 6.8 per cent.
Chloroform	Red	16.0	$2C_{19}H_{15}O_2N_3$, CH Cl ₃ requires loss, 15.9 per cent.
Pyridine	Yellow	10.5	$2C_{19}H_{15}O_2N_3$, C_5H_5 N requires loss, 1 1.1 per cent.

The *hydrochloride*, obtained from a hot glacial acetic acid solution, of the base by the addition of conc. HCl crystallises in glistening white rectangular plates, which melt with blackening at 280-290°. It is insoluble in water, and only sparingly soluble in boiling alcohol (Found : Cl, 9.9 ; $C_{19}H_{15}O_3N_2$, HCl requires Cl, 10.0 per cent.)

The *sulphate* separates in colourless crystals, on the addition of conc. H_2SO_4 to a hot solution of the base in glacial acetic acid. It melts with decomposition at 210-215° (Found : SO_4 , 13.2 ; $2C_{19}H_{15}O_2N_3$, H_2SO_4 , requires SO_4 , 13.1 per cent.).

Acetyl derivative.—Diphenyl-p-nitrobenzamidine (1 g.) was boiled with acetic anhydride (10 cc.) for about three hours and poured into water. The liquid was made alkaline with ammonia and kept over night ; the precipitated solid crystallised from alcohol in pale yellow prisms m.p. 155-156° (Found : N, 11.6 ; $C_{21}H_{17}O_3N_3$ requires N, 11.7 per cent.).

Benzoyl derivative.—The base (2 g.) was dissolved in pyridine (20 cc.) and benzoylchloride (1 g.) added. The addition of benzoyl chloride led to the separation of a white solid which was kept dissolved by keeping the mixture at about 110° for 3 hours. The mixture was poured into dilute sulphuric acid, when a pasty mass was precipitated which became solid on washing with water and ammonia. It crystallised from alcohol in pale yellow crystals m.p. 152-153° (Found : N, 10.0 ; $C_{26}H_{19}O_3N_3$ requires N, 10.0 per cent.).

Reduction.—By zinc and glacial acetic acid : The nitro compound (3 g.) was dissolved in hot glacial acetic acid (25 c.c.), zinc

dust (4 g.) was added in small portions during the course of one hour, at 100° with mechanical stirring. The mixture was filtered and the solution was diluted with much water and made alkaline with ammonia. The precipitated solid after two crystallizations from alcohol, was obtained in rectangular needles (0.5 g.) m.p. $196-198^{\circ}$ and this was not depressed by admixture with the base previously obtained by the author from aniline and carbon tetrachloride (*loc. cit.*).

2. With ammonium sulphide : The nitro-compound (4 g.) was dissolved in hot alcohol (50 c.c.), conc. ammonia (7 c.c.) added, and H_2S passed through the solution for about 1 hour at $60-70^{\circ}$. The residue after evaporation of the alcohol on the water bath was extracted twice with dilute HCl, the acid extract made alkaline with ammonia, and the precipitated solid crystallised from alcohol. The amino compound (1 g.) was obtained in colourless crystals m.p. $196-198^{\circ}$ in all respects identical with the substance already obtained. The salts and derivatives of this base have already been described. (*loc. cit.*).

p-Nitrobenz-p-toluidide.—This was prepared like p-nitrobenzani-
lide from p-nitrobenzoylchloride (92.5 g.) and p-toluidine (53.5 g.) in the presence of diethyl-aniline (75 g.) and crystallised from alcohol. Yield 102 g. It forms colourless silky needles, melting at $207-208^{\circ}$. Gattermann and Neuberg (*loc. cit.*) have described the substance as forming yellow crystals m.p. 198° . Lellmann and Hailer describe it as grayish yellow needles m.p. 203° (*Ber.*, 1893, 26, 2759). It is sparingly soluble in benzene, chloroform, acetone and cold alcohol and easily in hot alcohol and hot glacial acetic acid.

p-Nitrobenz-p-toluidide-imidochloride.—The hot liquid, obtained by heating together p-nitrobenz-p-toluidide (51 g.) and phosphorous pentachloride (45 g.) until hydrogen chloride ceased to be evolved, was poured into petroleum ether. The precipitated imido chloride was filtered off, and recrystallised from hot petroleum ether (b.p. $80-100^{\circ}$) when deep yellow plates were obtained. The crystals were kept in a desiccator over solid paraffin and solid KOH before analysis. It melts at 120° , and is easily soluble in benzene and ether and hot petroleum ether. For analysis, it was heated with sodium ethoxide in absolute alcoholic solution on the water-bath, water added, as much as possible of the alcohol evaporated, and the halogen in the cooled filtered solution estimated in the usual way (Found : Cl, 12.7 ; $C_{14}H_{11}O_2N_2Cl$ requires Cl, 12.9 per cent.).

A number of experiments on the action of phosphorous pentachloride on the p-toluidide were carried out under different condi-

tions. But in no case was any substance other than the imidochloride isolated.

Phenyl-p-tolyl-p-nitrobenzamidine.—This was prepared in two ways :—

(1) The above imido-chloride (55 g.) was treated with aniline (20 g.) in the presence of diethylaniline (60 g.) similarly to the preparation of diphenyl-*p*-nitrobenzamidine. The white hydrochloride obtained was moistened with a little alcohol and ground in a mortar with concentrated ammonia. The red solid obtained was crystallised from boiling alcohol containing a little ammonia. Yield—54 g.

(2) *p*-Nitrobenzanilide-imido chloride (10 g.), diethylaniline (8 g.), and *p*-toluidine (4.5 g.), gave by the usual method deep red crystals (9 g.) identical in all respects with the substance obtained from *p*-nitro-benz-*p*-toluidide imido-chloride and aniline.

Phenyl-*p*-tolyl-*p*-nitrobenzamidine crystallises from hot alcohol in scarlet needle-shaped crystals, which contain alcohol of crystallisation. For analysis, the substance was crystallised from acetone and the crystals heated at 100–110° to a constant weight. The brick-red powder melts at 138°. It is easily soluble in hot alcohol, benzene, acetone, chloroform and carbon tetrachloride, and from some of these it separates with solvent of crystallisation (Found : N, 13.0 ; $C_{20}H_{17}O_2N_3$ requires N, 12.7 per cent.).

The *hydrochloride* prepared in acetic acid solution crystallises in colourless needles and melts with decomposition at 290–300°. It is insoluble in water, sparingly soluble in hot alcohol, and easily in hot glacial acetic acid (Found : Cl, 9.6 ; $C_{20}H_{17}O_2N_3 \cdot HCl$ requires Cl, 9.7 per cent.).

The *sulphate* is prepared similarly. It can also be prepared in aqueous solution by boiling a suspension of the base in water, and adding dilute H_2SO_4 . The hot solution on cooling deposits yellow crystals, which melt with decomposition at 270–275°. It is slightly soluble in hot water, and much more soluble in other solvents than the hydrochloride (Found : SO_4 , 13.1 ; $2 C_{20}H_{17}O_2N_3 \cdot H_2SO_4$ requires SO_4 , 12.6 per cent.).

The *benzoyl derivative* was prepared by the pyridine method as before. It crystallises from alcohol in yellow needles m.p. 157–158° (Found : N, 9.6 ; $C_{27}H_{21}O_3N_3$ requires N, 9.7 per cent.).

Di-p-tolyl-p-nitrobenzamidine.—p.-Nitrobenz-p-toluidide-imido-chloride (28 g.) when treated with p-toluidine (12 g.) and di-ethylaniline (30 g.) by the usual method, gave 26 g. of the pure crystallised product. It crystallises from alcohol in orange-red crystals. For analysis, it was crystallised from acetone, and the crystals dried at constant weight at 100-110°. It melts at 160° and dissolves easily in hot alcohol, benzene, chloroform, carbon tetrachloride, and acetone. When crystallised from some of these, it contains solvent of crystallisation (Found : N, 12.4 ; $C_{21}H_{19}O_2N_3$ requires N, 12.2 per cent.).

The *hydrochloride* crystallises from glacial acetic acid in colourless crystals, which do not melt even at 300°. It is sparingly soluble in most solvents (Found Cl, 9.2 ; $C_{21}H_{19}O_2N_3$, HCl requires Cl, 9.3 per cent.).

The *sulphate* crystallised either from glacial acetic acid or aqueous solution, in yellow crystals, m.p. 198-201° (Found : SO_4 , 12.6 ; $2C_{21}H_{19}O_2N_3$, H_2SO_4 requires SO_4 , 12.2 per cent.).

The *benzoyl* derivative crystallised from alcohol in yellow crystals melting at 163-164° (Found : N, 9.3 ; $C_{28}H_{23}O_3N_3$ requires N, 9.3 per cent.).

Received July 20, 1936.

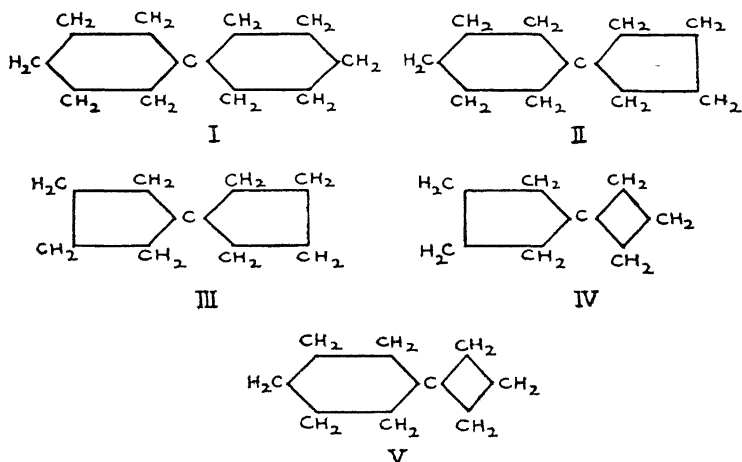
A NEW SYNTHESIS OF CYCLOHEXANE-SPIRO-CYCLOPENTANE

By

R. D. DESAI and M. A. WALI

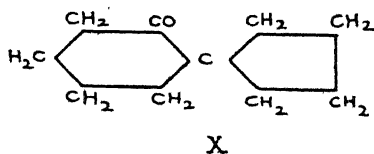
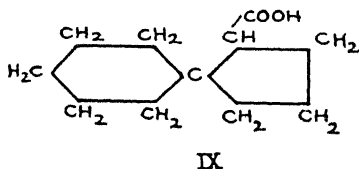
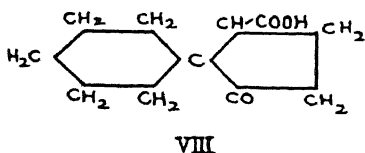
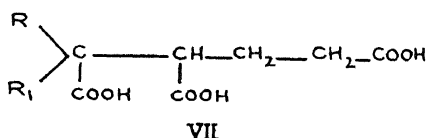
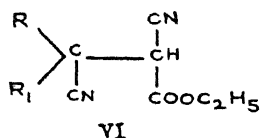
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Indisputable evidence in favour of the *valency-deflexion* hypothesis has, so far, come from physico-chemical sources, e.g., the dissociation constants of β - β -disubstituted glutaric acids, etc. (Spiers and Thorpe, *J.*, 1925, 538. Ives, Linstead and Riley, *Ibid.*, 1932, 1093. Gane and Ingold, *Ibid.*, 1928, 1594, 2267; 1929, 1691; 1931, 2153) as the purely chemical evidence has been, sometimes, found to be contradictory (Desai, *J.*, 1932 1047). It was thought that the values of heat of combustion of spiro-hydrocarbons (represented by formulae I-V) might furnish some useful data in calculating the relative strain in these systems, and, therefore, their syntheses were undertaken.



The present communication describes one method of synthesising cyclohexane-spiro-cyclopentane (II). The starting material was the ester represented by the formula (VI), (R R_1 = cyclohexane ring) obtained from cyclohexanonecyanohydrin and ethyl sodiocyanoacetate by Higson and Thorpe's method (*J.* 1906, 89, 1455). Acid hydrolysis of the condensation product of β -Iodopropionate and the sodium derivative of (VI) gave 1-carboxy cyclohexane-1 α -glutaric

acid (VII). Its open-chain analogue (where $R, R_1 = \text{Me}, \text{Me}$) has already been prepared by Perkin and Thorpe (*J.*, 1904, 85, 128). When the ring-closure was carried out by the method of Perkin and Thorpe, cyclohexane-spiro-cyclopentane-2-one-5-carboxylic acid (VIII) was obtained. Its clemmenson reduction gave cyclohexane-spiro-cyclopentane-5-carboxylic acid (IX), but as it was not possible to obtain it in a solid form, the distillation of a mixture of its calcium salt with soda-lime gave the desired cyclohexane-spiro-cyclopentane (II) which was characterised by the formation of its tetrabromo-derivative. The same spiro-hydrocarbon was prepared and characterized by Zelinsky and Schuikin (*Ber.*, 1929, 62, 2180) by treating the hydrazone of Meiser's pinacolin (*Ber.*, 1899, 32, 2055) with platinum and caustic potash, and by Clemo and Ormston (*J.*, 1933, 353) by the Clemmenson reduction of 2-keto-cyclohexane-*spiro*-cyclopentane (X) obtained by the method of Hückel and co-workers (*Ann.*, 1929, 474, 121).



EXPERIMENTAL

Ethyl-1-cyano-cyclohexane-1-α-cyano-glutarate.—To the semi-solid mass of the sodium derivative of 1-cyclohexane-1-cyano-acetate ($\frac{1}{2}$ mol.) prepared according to Kandiah (*J.*, 1932, 1224), ethyl β -Iodopropionate (80 g.) was gradually added with constant shaking and cooling under the tap. After allowing it to stand at ordinary temperature for three hours, the mixture was heated for nearly 24 hours, when it became neutral. After diluting it with much water, the precipitated oil was extracted with ether, washed, dried, recovered and distilled, when the desired product ethyl-1-cyano-cyclohexane-1- α -cyano glutarate passed over as a viscous liquid boiling at 225-

232|15 mm. and on redistillation boiled at 227-228|15 mm. (yield variable 25-40 per cent.). (Found C, 63.5; H, 7.6; $C_{17}H_{24}O_4N_2$ requires C, 63.7; H, 7.5 per cent.).

Hydrolysis of the ester could not be carried out satisfactorily by Conc. HCl. The ester (25 g.) was dissolved in Conc. H_2SO_4 (25 c.c.) and kept overnight. Water was added till permanent turbidity was produced, and the mixture was heated on sand bath under-reflux for 24 hours. After diluting with water the acid was extracted with ether, purified through sodium carbonate, and kept in a vacuum. As it did not show the tendency to solidify, it was mixed with absolute alcohol (60 c.c.) and Conc. H_2SO_4 (6 c.c.), and heated under reflux for 24 hours. The ester was isolated in the usual manner and distilled when the *triethyl ester of 1-carboxy-cyclohexane-1- α -glutaric acid* boiled constantly at 174-175°|15 mm. (Found C, 63.0; H, 8.9; $C_{18}H_{30}O_6$ requires C, 63.1; H, 8.8 per cent.).

This ester was hydrolysed by aqueous-alcoholic alkali and *1-carboxy-cyclohexane-1- α -glutaric acid* isolated in the usual manner after saturating the solution with ammonium sulphate. It could be easily obtained in the solid, sandy form by adding Conc. HCl to its saturated aqueous solution and melted at 165-168° (efferv.) (Found C, 56.1; H, 7.1; $C_{12}H_{18}O_6$ requires C, 55.8; H, 6.9 per cent.).

Cyclohexane-spiro-cyclopentane-2-one-5-carboxylic acid :—

The dry sodium salt of 1-carboxy-cyclohexane-1- α -glutaric acid (50 g.) and acetic anhydride (50 cc.) were mixed in a 500 cc. round bottom flask fitted with a long condenser tube. The flask was gradually heated in an oil-bath which was maintained at 130-140° for about 8 hours, when the evolution of carbon dioxide was almost over. After removing most of the acetic anhydride under reduced pressure, absolute ethyl alcohol (200 c.c.) Conc. H_2SO_4 (50 c.c.) were added, and the mixture heated for 8 hours. After dilution with water, the precipitated oil was extracted twice with ether, washed, dried and recovered. *Ethyl cyclohexane-spiro-cyclopentane-2-one-5-carboxylate* boiled at 140-145°|15 m.m. leaving some residue. On redistillation, it boiled at 141-142°|15 m.m. (Found : C, 70.8; H, 7.3; $C_{13}H_{20}O_3$ requires C, 70.5; H, 7.4 per cent.).

The *semicarbazone* prepared in the usual manner crystallised from alcohol in needles m.p. 203° decomp. (Found : C, 59.7; H, 8.1; $C_{14}H_{23}O_3N_3$ requires C, 60.0; H, 8.2 per cent.).

Cyclohexane-spiro-cyclopentane-2-one-5-carboxylic acid obtained by the hydrolysis of the ethyl ester with aq-alcoholic NaOH, solidi-

fied when kept in vacuum and crystallised from a mixture of benzene and petrol in needles m.p. 104-105° (Found, C, 67.2; H, 8.0; $C_{11}H_{16}O_3$ requires C, 67.4; H, 8.1 per cent.).

Cyclohexane-spiro-cyclopentane.—The keto-carboxylic acid (3 g.), amalgamated zinc (15 g.) and Conc. HCl (25 c.c.) were refluxed for 24 hours. The resulting product floating as a waxy mass was extracted with ether, dried and kept in a desiccator, but failed to solidify. The mixture of its calcium salt and soda lime (equal amount) was subjected to slow heating in an oil-bath under reduced pressure. Much decomposition occurred, and an oily liquid distilled over. This was taken up in ether, washed with a solution of sodium carbonate, dried and distilled when it boiled at 70-75°/15 m.m. The tetrabromide, prepared according to the method of Zelinsky and Schuikin (*loc. cit.*) melted at 131-132° (Found: Br, 70.8, Calc. for $C_{10}H_{14}Br_4$, Br = 70.5 per cent.).

Received July 28, 1936.

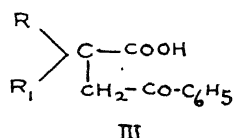
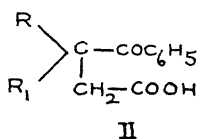
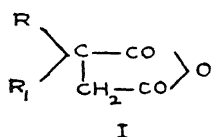
THE CONDENSATION OF SUCCINIC ANHYDRIDE WITH α -AND β -NAPHTHYL METHYL ETHERS

By

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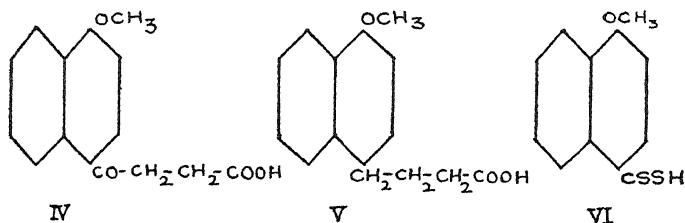
Muslim University, Aligarh.

For some times past, we have been studying the condensation of the anhydride of α -disubstituted succinic acids (I, where R, R₁ = C₆H₅, H, or Me, Me, or cyclohexane or cyclopentane rings) on benzene and its simple substitution products, in presence of anhydrous AlCl₃, and the results have shown that it is possible to prepare isomeric γ -ketonic acids (II and III) according to different experimental conditions. (Unpublished work). While applying this reaction to substituted naphthalenes, complications arose owing to the uncertainty of the position taken up by the acid residue in the naphthalene nucleus. To clear up this issue, the condensation of succinic anhydride with α - and β -naphthyl methyl ethers was studied using nitrobenzene and carbon disulphide as solvents. Although the results are far from complete, the publication of a paper by Short, Stromberg and Wiles (*J.*, 1936, 319) has necessitated the publication of the results obtained by us.

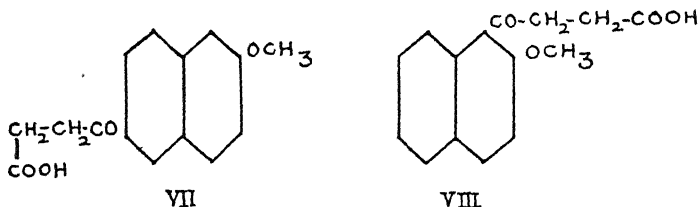


α -Naphthyl methyl ether reacted with succinic anhydride in nitrobenzene solution to give β -(4-methoxy-1-naphthoyl) propionic acid (IV) which yielded, with considerable difficulty, γ -(4-methoxy-1-naphthyl) butyric acid (V) on Clemmensen reduction. The constitution of the acid (V) is beyond doubt as it has been synthesised by Kon and Ruzicka (*J.* 1936, 192) by unambiguous method. In presence of Carbon disulphide, however, a thioacid m.p. 225° was also formed, besides the acid (IV) which was the main product. The thioacid has been provisionally assumed to have the constitution represented by formula (VI).

β -Naphthyl methyl ether gave mainly the acid m.p. 148° accompanied by an isomeric acid m.p. $136-137^\circ$ in presence of nitrobenzene. The former was shown to be β -(6-methoxy-2-naphthoyl)



propionic acid (VII), as it was oxidised by sodium hydrobromite to 6-methoxy- β -naphthoic acid (Fries & Schimmelschmidt, *Ber.*, 1925, 58, 2835; also Haworth and Sheldrick, *J.*, 1934, 864). The low melting acid proved to be β -(2-methoxy-1-naphthoyl) propionic acid (VIII), which was also the main product if the condensation was brought about in presence of carbon disulphide. A small quantity of a thio-acid was also formed, but this could not be obtained in sufficient purity. Fieser and Peters (*J. Amer. Chem. Soc.* 1932, 54, 4351) obtained an acid m.p. 152° by condensing succinic anhydride with β -naphthyl methyl ether in presence of nitrobenzene. These investigators supposed it to be β -(2-methoxy-1-naphthoyl)-propionic acid, but it is possibly identical with acid (VII). We are busy studying the constitution of the thio-acids obtained in these condensations. The formation of thio-acids during the Friedel-Crafts condensations using carbon disulphide as the solvent has also been noticed by Jörg in the case of phenetole (*Ber.*, 1927, 60, 1466).



EXPERIMENTAL

β -(4-Methoxy-1-naphthoyl)-propionic acid (IV).—Succinic anhydride (10g.) was slowly added to a cooled solution of AlCl_3 (22g.) in nitrobenzene (75 c.c.). After adding α -naphthyl methyl ether (16g.) slowly with constant shaking and cooling, the mixture was set aside for 48 hours. After decomposing the aluminium chloride with dilute HCl, and steam-distilling off the nitrobenzene, the precipitated solid

was removed and purified through sodium carbonate. It crystallised from dilute alcohol in needles m.p. 177-178° (Found : C, 69.7 ; H, 5.6. Equv.=260. $C_{15}H_{14}O_4$ requires C, 69.8 ; H, 5.4 per cent. equivalent=258). The yield of the acid is improved if the mixture is worked up after 100 hours, but it is considerably difficult to purify the later fractions during crystallisations. There is an indication of the formation of an isomeric acid, but we have not been able to isolate it in a pure condition so far.

γ -(4-methoxy-1-naphthyl)-butyric Acid (V).

A mixture of the keto-acid (2g), amalgamated zinc (10g.) and concentrated HCl (25) was heated on sand-bath under reflux for 24 hours. The viscous mass obtained on cooling was purified through sodium carbonate. The oily acid slowly solidified to a cake, and crystallised from dilute alcohol in minute plates m.p. 131° (Found, C, 73.5 ; H, 6.8. Calc. for $C_{15}H_{18}O_3$, C, 73.7 ; H, 6.6 per cent.).

Condensation of α -naphthyl methyl ether with succinic anhydride in presence of carbon disulphide, and isolation of 4-methoxy-1-thionaphthoic acid. (VI).

Powdered $AlCl_3$ (22g.) was slowly added to a cooled mixture of succinic anhydride, (10g), α -naphthyl methyl ether (16g.) and carbon disulphide (50 c.c.) with constant shaking and cooling. After keeping the mixture at ordinary temperature for 24 hours, it was gently heated on waterbath under reflux for 8-10 hours. Much of the solvent was removed under the fan, aluminium chloride was decomposed by HCl, and the resulting semi-solid mass purified through sodium carbonate. The solid was fractionally crystallised from dilute alcohol which left a residue unmelted below 300°. The first fraction melted at 165-170°, but the m.p. could be raised to 176-177° by recrystallisation, and this was unaltered by admixture with a sample prepared by using nitrobenzene. The second fraction melted at 150-160° ; while the mother-liquor, on concentration, gave a brown solid melting at 190-205°. This was recrystallised from alcohol (charcoal) when pale-yellow needles m.p. 225° were obtained (Found ; S = 30.8, Equv. 209. (monobasic). $C_{12}H_{10}OS_2$ required S=30.5 per cent ; equiv. =210).

Condensation of β -Naphthyl methyl ether, and Succinic anhydride.

As the general procedure is exactly similar to that of the α -analogue, unnecessary details are omitted. Using nitrobenzene as the solvent, the reactants are taken in the proportion as described for α -

naphthyl ether. If the mixture is worked up after 48 hours, β -(6-methoxy-2-naphthoyl) propionic acid (VII) is not much contaminated by the isomeric β -(2-methoxy-1-naphthoyl)-propionic acid, which seems to be formed during the later stage of the reaction. After two crystallisations from dilute alcohol, the first acid was obtained pure in needles m.p. 147-148°. Its oxidation to 6-methoxy-2-naphthoic acid can also be brought about by sodium hypobromite. Its analysis as well as other details are omitted as they are described by Short, Stromberg and Wiles (*loc. cit.*).

β -(2-methoxy-1-naphthoyl)-propionic acid (VIII) can be obtained in a pure form by using carbon disulphide as the solvent. The alcoholic mother-liquor, after the removal of the acid, which crystallised in flat needles m.p. 137°, left a gummy residue containing sulphur, but nothing definite could be isolated.

Received, August 15, 1936.

MEASUREMENT OF THE HYDROGEN ION CONCENTRATION BY MEANS OF THE GLASS ELECTRODE

By

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When a thin glass membrane separates two solutions having different hydrogen ion concentration, a difference of potential, proportional to the difference in the pH values of the two solutions, is set up between the two sides of the membrane. This fact forms the basis of methods in which the glass electrode is used to measure the pH. The latest developments in the technique of these methods have made it possible to use the glass electrode method as the most convenient, expeditious and accurate for acidic as well as for strongly alkaline solutions.

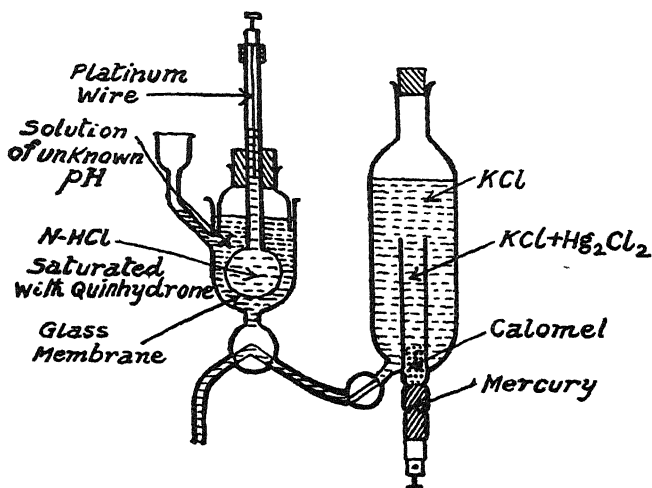


Fig. 1.

The quality of glass used for the membrane plays an important part and the question has been investigated in detail by McInnes and Dole (*J. Amer. Chem. Soc.*, 1930, 52, 29). Morton (*J. Scientific Instruments*, 1930, 7, 187) used membranes in the form of bulbs prepared from a highly conducting glass containing sixty per cent. silica, thirty per cent. sodium carbonate and ten per cent. calcium carbonate. Similar bulbs supplied by the Cambridge Instrument Company, London, were used by the author. The Morton glass electrode cell is reproduced in figure 1.

The measurement of the e. m. f. of a glass electrode system is rendered difficult on account of the high resistance of the glass membrane. The current produced is too small to permit the use of a capillary electrometer or a sensitive galvanometer in the ordinary potentiometric method of measuring e. m. f. This difficulty has been overcome by discharging condensers of suitable capacity through a very sensitive ballistic galvanometer (cf. Morton, *loc. cit.*) or by the use of a quadrant electrometer as a null point instrument. (cf. Kerridge, *J. Scientific Instruments*, 1926, 3, 404). These methods require elaborate screening and high insulation and are subject to an error of ± 4 millivolts. (Britton, *Hydrogen Ions*, 1932, p. 132.)

Several investigators (Goode, *J. Amer. Chem. Soc.*, 1922, 44, 26; Morton, *Pharm. J.*, 1927, 118, 761; Stadie, *J. Biol. Chem.*, 1929, 83, 477 and others) have used thermionic valves for the purpose but these methods involve the passage of small grid currents through the cell which may cause sufficient polarisation to make them incapable of being very accurate.

Harrison (*J. C. S.*, 1930, 1530) used a valve called the electrometer triode, the essential feature of which is that the grid current is of the order 10^{-14} ampère. On account of this the anode current

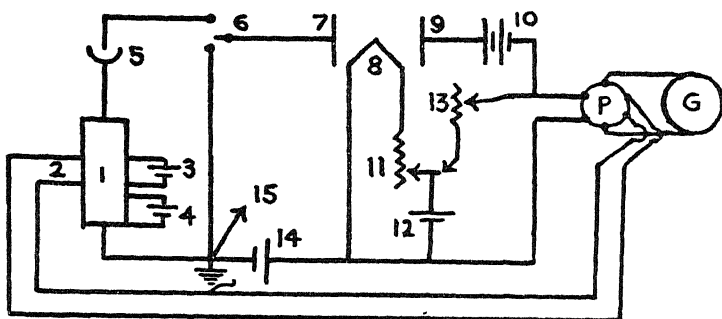


Fig. 2.

1. Potentiometer; 2. Leads to G. T.; 3. St. cell; 4. P. C.; 5. Glass electrode; 6. Switch; 7. Grid; 8. Filament; 9. Anode; 10. Anode battery; 11. Variable resistance 15 ohms; 12. Filament battery; 13. Variable resistance 50,000 ohms; 14. Grid battery; 15. Earth connection; P. Pohl commutator; G. Galvanometer.

does not vary on the introduction of a high resistance such as that of a glass membrane in the grid circuit, which, however, is the case with ordinary valves. Harrison's circuit has been improved upon by Greville and Maclagan (*Trans. Farad. Soc.*, 1931, 26, 210).

For the measurement of the hydrogen ion concentration of certain strongly alkaline solutions of the alkali salts of weak acids which are

being investigated by the author the Morton type glass electrode system in conjunction with the electrometer triode circuit of Greville and Maclagan was used with suitable modifications. Since sufficient details of working and construction of the valve unit are not available in the published papers they are given below. The circuit diagram is shown in figure 2 with necessary details.

The valve used by the author was Philips 4060 having the following characteristics:—

V_f = Filament voltage = 0.90 volt.

V_a = Maximum anode voltage = 4.00 volts.

I_g = Grid current (maximum) = 10^{-14} ampere.

S = Mutual conductance or slope (maximum) = 0.028 MA/V.

One of the improvements made by Greville and Maclagan (*loc. cit.*) on Harrison's circuit consists in the use of a switch of special design. The present author has constructed a switch of new design which is more robust and easy to construct than the one described by Greville and Maclagan (*loc. cit.*). It was constructed as follows:—

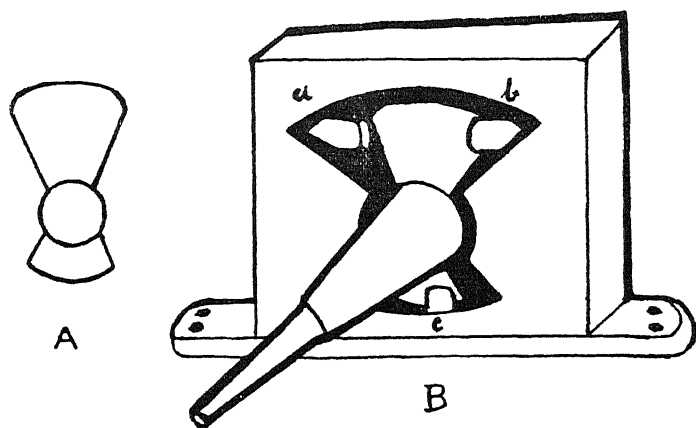


Fig. 3.

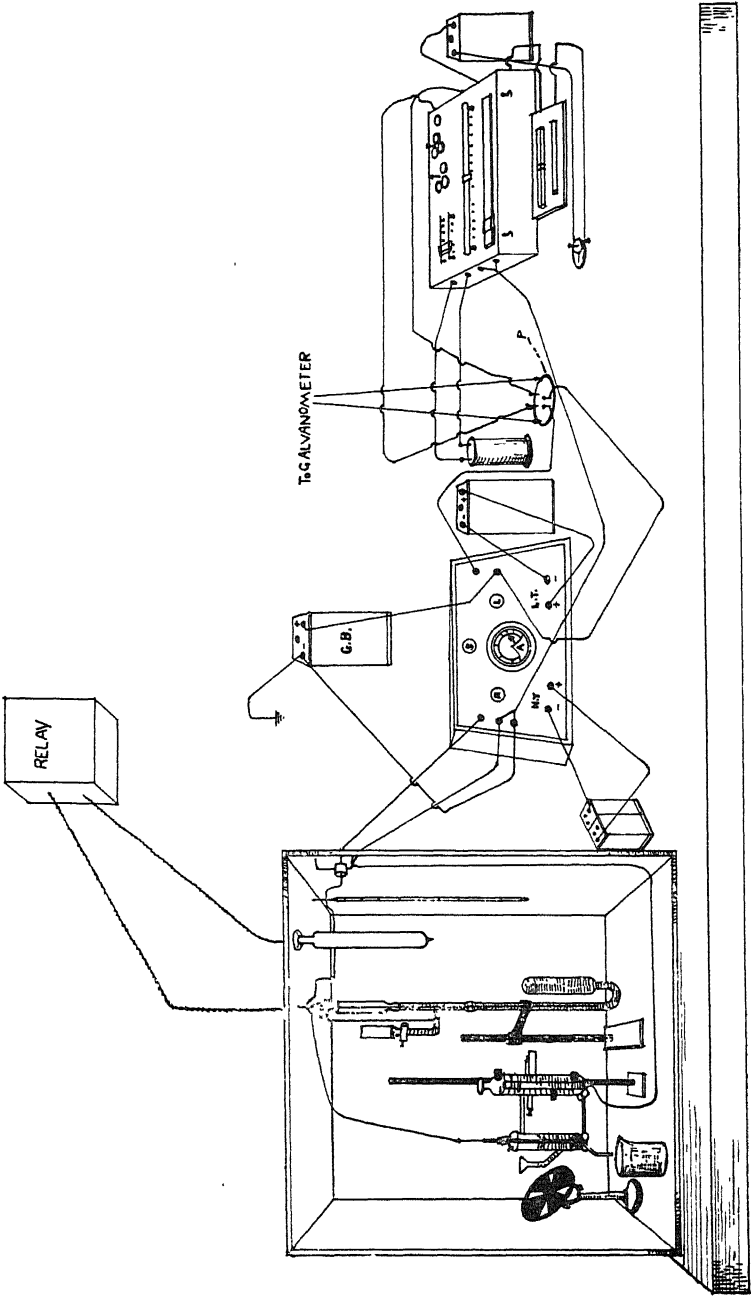
A brass metal piece 2 mm. thick was cut into the shape shown in figure 3A. It was fixed to an ebonite rod the rotation of which enabled it to be moved either clockwise or anti-clockwise. The metal strip was placed inside an ebonite block in the manner shown in figure 3B, in which a, b, c, are brass clips which hold the metal strip tightly. When turned to the extreme clockwise position the strip connects the terminals at b and c while when turned to the ex-

treme anti-clockwise direction it connects the terminals at a and c. In the central position all the three terminals are connected and thus the object of making the second circuit before the first is broken is achieved. This switch has been in use for nearly two years and with occasional cleaning has given entire satisfaction.

The valve, the resistances and the switch were enclosed in a wooden box the inside of which was lined with tin foil. The ebonite terminals, the knobs of the switch and the resistances, as well as an ammeter, were all mounted on an ebonite panel. The valve was shielded by means of a tin can which, together with the tin foil of the box, was earthed. The shielding of the valve is an important factor, for, the current flowing in the anode circuit becomes steady within a shorter time than without it. The earth connection is made to the grid bias minus (vide, Greville and MacLagan) and not to grid bias plus as is done in Harrison's original circuit.

The assemblage of the apparatus is shown in figure 4. A Tinsley moving coil galvanometer (not shown in the diagram) having a sensitivity of 12 mm. per millivolt at one meter was used. An ebonite Pohl commutator with its wires for reversing the current removed (P in figure 4) was substituted for the jacks used by Greville and MacLagan (*loc. cit.*).

To test the valve unit a standard Weston cell was introduced in place of the glass electrode system and its e. m. f. measured in the following manner : After the necessary connections were made the filament current was switched on by turning the knob L and with the knob S in the extreme clockwise position. It was kept constant at about 0.9 ampere throughout. The potentiometer having been standardised its galvanometer connections were short circuited and the galvanometer was put in the anode circuit. By turning the knob R the deflection of the galvanometer was adjusted to a suitable position on the scale. The potentiometer was next put in the circuit of the unit the initial reading of the galvanometer noted and the knob S turned gradually to the extreme anti-clockwise position. The galvanometer reading which thus changed was brought back to the initial reading by applying a known e. m. f. from the potentiometer. The potentiometer reading gave the e. m. f. that was being measured. After making this measurement a high resistance was introduced in the circuit of the Weston cell and its e. m. f. determined a second time. If the e. m. f. remained unaltered it was considered that there was no leakage. A grid bias of two volts was found to be the most satisfactory after trials with higher and lower values.



The glass electrode system was standardised by means of buffer solutions of known pH. Two such solutions were used viz : M|20 potassium hydrogen phthalate (pH 3.97) and M|20 borax (pH 9.15). The former was prepared according to the method of Dodge (*J. Ind. Eng. Chem.*, 7, 29; *J. Amer. Chem. Soc.*, 42, 1655), described by Clark ("Determination of Hydrogen Ions," 1928, p. 194), and the latter was Merck's G. R. quality. For this purpose the Morton glass cell was placed in an electrically heated air thermostat which was zinc-lined and earthed. The calomel half-cell was cleaned and refilled from time to time. From the observed e. m. f. at 30°C the pH was calculated by means of the equation.

$$\text{pH} = \frac{0.4535 - E}{0.06}$$

In connection with the above glass electrode method of determining pH the following points are noteworthy :

- (i) Accumulators need to be fully charged and all connections securely made.
- (ii) An asymmetric potential of several millivolts is developed by the glass electrode if it is allowed to get dry : it can be brought back to its original state by keeping it in a buffer solution or preferably in a solution of dilute hydrochloric acid. Certain bulbs retain the asymmetric potential when allowed to dry for several days and have to be discarded.
- (iii) An electro-static field such as generated by an X-ray tube in the vicinity of the valve affects the reading.
- (iv) The earth connection must be made by proper connections to a water tap.

The author takes this opportunity to thank the University of Bombay for a grant from which part of the expenses on the construction of the valve unit were defrayed.

Received, 15th August, 1936.

THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS CONTAINING SODIUM HYDROXIDE AND PHOSPHORIC ACID

By

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Filhol and Senderens (*Compt. Rend.*, 93, 388) reported the isolation of $(P_2O_5)_2 \cdot 3 NaOH \cdot H_2O$ from a neutral solution containing one and a half equivalents of sodium hydroxide and one equivalent of phosphoric acid. They also obtained crystals of the composition $NaH_2PO_4 \cdot Na_2HPO_4 \cdot 3H_2O$ from an aqueous solution of sodium hydroxide and phosphoric acid made neutral to litmus. (Cf. *Compt. Rend.*, 94, 649). Joulie (*Compt. Rend.*, 1902, 134, 604) obtained crystals of $Na_3H_3(PO_4)_2$ by adding sufficient phosphoric acid to a solution of disodium hydrogen phosphate till it was neutral to litmus and then heating it to $45^\circ-50^\circ C$. An acid salt having the formula $NaH_2PO_4 \cdot H_3PO_4$ has been described by Giran (*Compt. Rend.*, 1902, 134, 711) and Parker (*J. Phys. Chem.*, 1914, 18, 653) has obtained $KH_2PO_4 \cdot H_3PO_4$ as a solid phase during a phase rule study of the system potassium hydroxide-phosphoric acid-water. Smith (*J. Soc. Chem. Ind.*, 1917, 36, 420) found that phosphoric acid neutralised by sodium hydroxide or sodium carbonate with a view to get disodium hydrogen phosphate can be caused to crystallise with great difficulty. He claimed to have isolated salts containing Na_3PO_4 and Na_2HPO_4 in the proportions : (i) 1 : 17 (ii) 1 : 8 (iii) 1 : 6 (iv) 1 : 3 (v) 3 : 2 (vi) 2 : 3 (vii) 1 : 2 and (viii) 18 Na_3PO_4 : Na_2O .

The isolation of the basic and acid salts described above lacks confirmation. Further, a search of the literature shows that no attempt has so far been made to investigate the existence of these salts in solution. The present investigation was, therefore, undertaken to investigate the nature of solutions containing sodium hydroxide and phosphoric acid in varying proportion and the present paper contains data on the measurement of the electrical conductivity of such solutions.

Several workers have measured the electrical conductivity of solutions of phosphoric acid and of those of sodium phosphates at different temperatures (vide : Mellor, *A Treatise on Inorganic and Theoretical Chemistry*, 8, 956 ; *ibid.*, 2, 849 and 855 : Gmelin, Teil 21,

905 and 910). In most of these investigations the concentrations used are fairly low and the data obtained have been utilised for finding the degree of ionisation, the values of k_1 , k_2 , and k_3 or the degree of hydrolysis of the sodium salts.

Adopting the idea first put forward by Kohlrausch (*Ann. Phys. Chem.*, 1885, 26, 225) that the end points in titration reactions may be determined by means of the conductance method certain investigators have collected data on the conductometric titrations of dilute aqueous solutions of phosphoric acid by means of sodium hydroxide—(Berthelot, *Compt. Rend.*, 113, 851; *Ann. Chim. Phys.*, 1893, (6) 28, 5; (Miss) Lanzig and Van der Walk, *Rec. trav. Chim.*, 1929, 48, 83; Kuster, Gruters and Geibel, *Z. Anorg. Chem.*, 1904, 42, 225; Thiel and Roemer, *Z. Physik. Chem.*, 1908, 63, 711; Schmidt, *Am. Chem. J.*, 1908, 40, 305; Kolthoff, *Z. Anorg. Chem.*, 1920, 112, 165; Davis, Oakes and Salisbury, *Ind. Eng. Chem.*, 1923, 15, 182). The results obtained have indicated the points of neutralisation corresponding to the dissociation of the first and the second hydrogen atoms of the acid: the tribasic alkaline phosphate is almost completely dissociated in dilute aqueous solutions.

EXPERIMENTAL

The electrical conductivity of aqueous solutions containing different amounts of sodium hydroxide and phosphoric acid expressed as the ratios of Na_2O and P_2O_5 in the proportions (i) 1.5 : 1, (ii), 0.9225 : 1, (iii) 1 : 1.5, (iv) 1 : 2, (v) 1 : 2.5 and (vi) 1 : 3 was measured for concentrations between 2 N and 0.005 N at 30°C. The temperature was kept constant by means of a water thermostat using a toluene regular within $\pm 0.05^\circ\text{C}$.

The electrical conductivity was measured by the method of Kohlrausch. The platinum electrodes of the conductivity cell were platinised according to the instructions given in "Physico-Chemical Methods" (Reilly, Rae and Wheeler, 1926 edition, p. 588). The cell constant was checked from time to time and was found to remain constant within limits of experimental error. The bridge wire was calibrated according to the method of Strouhal and Barus (*Wied. Ann.*, 1880, 10, 326) and the minimum point was detected by means of a sensitive ear-phone. Several readings were taken for the resistance of a solution and the mean of these, given in the tables was used for calculation.

For the preparation of solutions containing different ratios of Na_2O and P_2O_5 Merck's extra pure chemicals were used. The sodium hydroxide required for the purpose was prepared free from carbonate by dissolving it (100 grams) in water (100 c.c.) The solution thus

obtained was allowed to stand for 48 hours and then the supernatant liquid was filtered through a sintered bed Jena glass funnel.

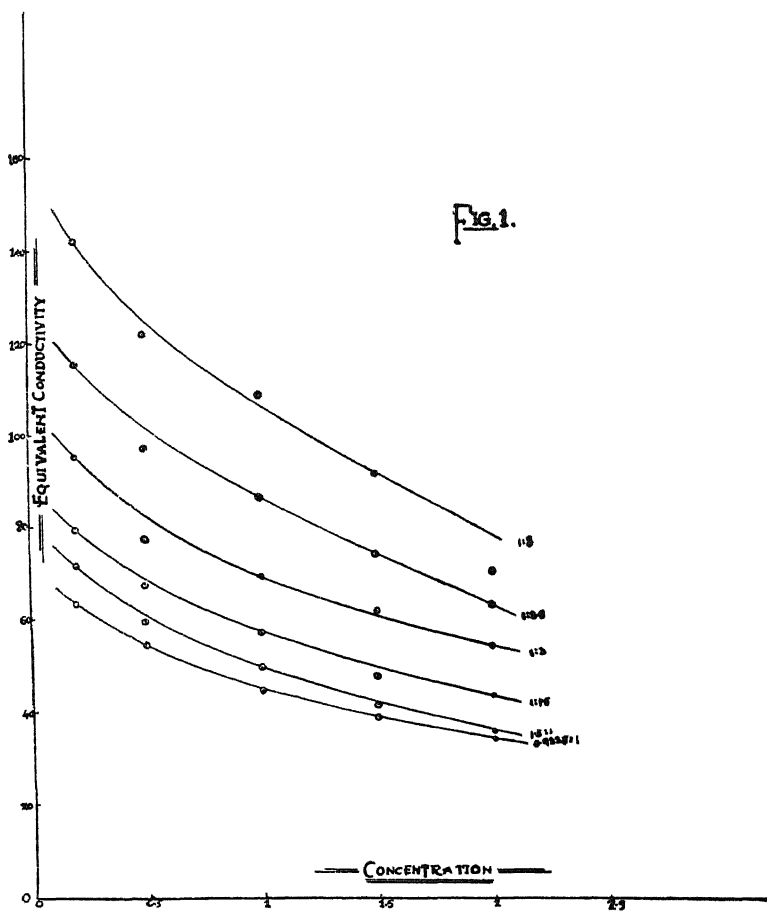
Ordinary distilled water, distilled over alkaline potassium permanganate using a Pyrex glass condenser, was used in the preparation of solutions. All the stock solutions were kept in Jena glass flasks in an atmosphere free from carbon dioxide.

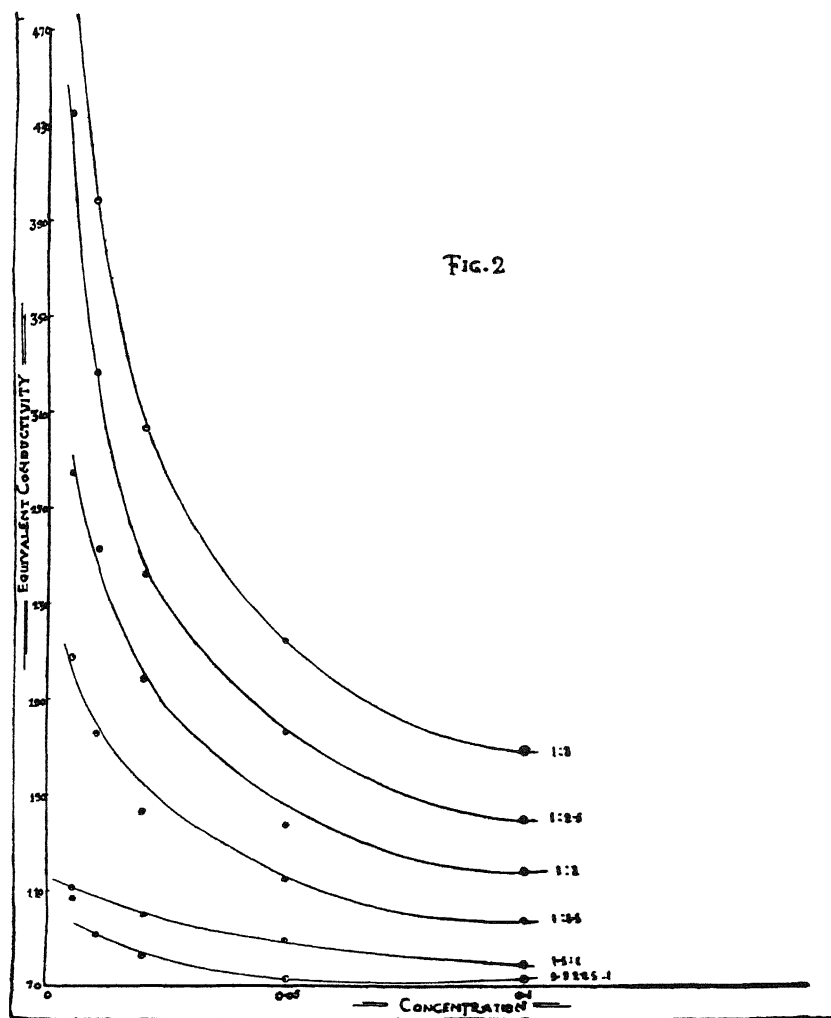
The burettes, pipettes, measuring flasks, weights etc. were standardised before use according to the standard methods (vide, "Physico-Chemical Methods", Reilly, Rae and Wheeler, 1926 edition).

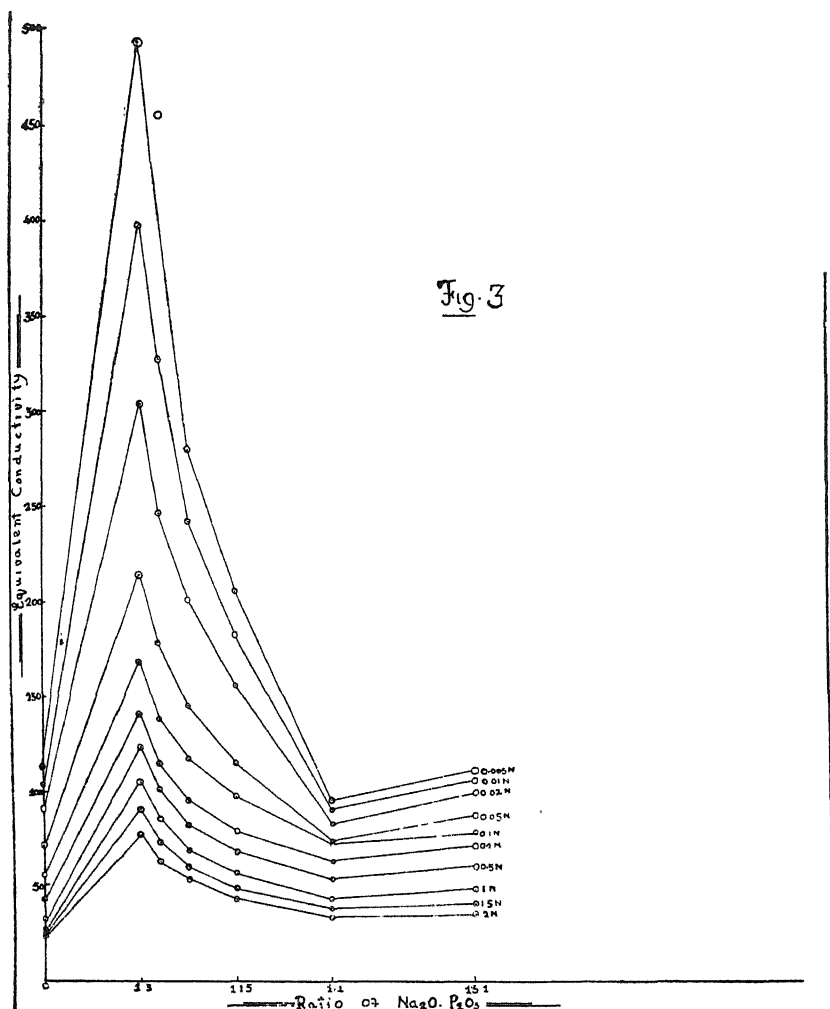
The results obtained are represented graphically in figures 1 to 3 in the first two of which the equivalent conductivity is plotted against concentration, and the third gives a plot of the equivalent conductivity against the ratios of $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$. The values for the latter were obtained from figures 1 and 2 and are given in the following table in which N=Normality of the solution in terms of its sodium content.

TABLE I.

N	Ratio of $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$					
	1 : 3	1 : 2.5	1 : 2	1 : 1.5	0.9225 : 1	1.5 : 1
2.0	77.5	62.5	53.5	42.94	33.45	35.1
1.5	91.0	73.6	60.0	49.0	38.48	41.15
1.0	105.8	86.0	69.0	57.0	44.4	49.35
0.5	124.5	101.5	82.5	68.5	54.6	60.6
0.2	142.0	115.35	95.35	79.8	63.4	71.85
0.1	168.6	139.5	118.1	97.79	72.73	78.83
0.05	214.8	179.0	146.0	116.0	74.0	88.0
0.02	304.2	247.0	202.0	157.0	83.0	100.0
0.01	398.0	327.6	243.0	183.0	91.64	107.0
0.005	493.4	455.8	280.0	206.0	95.5	111.6







DISCUSSION

It will be seen from figures 1 and 2 that the equivalent conductivity increases with dilution for all solutions containing different ratios of Na_2O and P_2O_5 used in this investigation. Two sets of curves have been drawn on separate graph papers for concentration range 2 N to 0.2 N and 0.1 N to 0.005 N for the sake of clarity. This effect of dilution on the equivalent conductivity is due to the increased ionisation or hydrolysis of the sodium salt or salts formed in these solutions. Either of these factors cause an increase in the number of ions in solution and hence there is an increase in conductivity.

Interesting results are obtained when the equivalent conductivity is plotted against the ratio of Na_2O and P_2O_5 . It will be noticed from these curves, which are shown in figure 3, that in solutions more dilute than 0.2 N the equivalent conductivity of solutions containing Na_2O and P_2O_5 in the ratio 1.5 : 1 is greater than that of those containing the ratio 1 : 1 (approximate). There is a distinct change of direction of the curves at points corresponding to the latter ratio. This increase in conductivity is not so well marked for concentrated solutions between 2 N and 0.2 N. It appears that this change of direction of the curves indicates the formation of NaH_2PO_4 and is in agreement with similar observations made by Harman (*J. Phys. Chem.*, 1925, 29, 1455) in connection with the formation of sodium silicate and by Prasad, Mehta and Joshi (*J. Ind. Chem. Soc.*, 1930, 7, 973) while inferring the formation of sodium aluminate.

The increased equivalent conductivity of solutions containing Na_2O and P_2O_5 in the ratio 1.5 : 1, particularly in dilute solutions, is due to an increase in the number of mobile hydroxyl ions. But it can also be assumed that a certain proportion of the salt Na_2HPO_4 is formed in these solutions : at high dilutions this salt is largely hydrolysed and hence the solutions behave merely as those containing a mixture of NaH_2PO_4 and NaOH . At low dilutions the degree of hydrolysis is reduced and, as observed, the increase in equivalent conductivity is not great.

If the points on the curves between the ratios 1 : 3 and 1 : 1 (approx.) are joined by straight lines as done by Harman (*loc. cit.*) a change of direction is noticed in concentrated solutions, not less concentrated than 0.2 N, at points corresponding to the ratios 2 : 3, 1 : 2 and 2 : 5. If it be assumed that the change of direction of these curves indicates the formation of definite salts as in the case of the formation of NaH_2PO_4 , the formation of $2\text{NaH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$ and $2\text{NaH}_2\text{PO}_4 \cdot 3\text{H}_3\text{PO}_4$ must be postulated. Of these salts $\text{NaH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$ has been isolated by Giran (*loc. cit.*) and a corresponding salt of potassium has been reported by Staudenmaier (*Z. Anorg. Chem.*, 1894, 5, 383) and Parker (*loc. cit.*). However, there is no *a priori* reason why these points should not be joined to give a smooth curve in which case no breaks will be observed and the formation of the above mentioned salts held improbable.

The remarkable change of direction of the curves at points corresponding to the ratio 1 : 3 cannot be taken to indicate the formation of a definite salt because these points are merely joined to those corresponding to the equivalent conductivity of pure phosphoric acid, the ratio for which is 0 : 1. This part of the curve simply shows that the conductivity of pure phosphoric acid is increased considerably by

the addition of sodium hydroxide and that after reaching a maximum value it falls fairly rapidly at first and then more slowly on the addition of increasing amounts of sodium hydroxide until it attains a minimum value corresponding to the formation of monosodium dihydrogen phosphate.

Received 15th August 1936.

HYDROGEN ION CONCENTRATION OF SOLUTIONS CONTAINING SODIUM HYDROXIDE AND PHOSPHORIC ACID

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The determination of hydrogen ion concentration has received increasing attention during recent years as it affords an important method for the study of acid-base equilibria. In continuation of the work described in the preceding communication (this Journal, pp. 83-90) the hydrogen ion concentration of solutions containing sodium hydroxide and phosphoric acid in different proportions was determined using the glass electrode together with the electrometer triode.

The literature on the subject contains data which may be divided under two heads (*a*) potentiometric titration of solutions of phosphoric acid by means of sodium hydroxide and (*b*) determination of the pH of phosphate buffer mixtures or of solutions containing phosphates of the alkali metals.

(*a*) Using the hydrogen electrode Prideaux (*J. C. S.* 1911, T, 1224) measured the hydrogen ion concentration of solutions of sodium phosphate containing different ratios of milligram molecules of sodium hydroxide to ten of phosphoric acid and compared the results with those obtained by Salm (*Z. Physikal. Chem.*, 1907, 57, 492). By means of the same method Hoffmann and Gortner (*J. Phys. Chem.*, 1925, 29, 770) followed the titration of phosphoric acid by sodium hydroxide and found that the titration curve they obtained was similar to the one obtained by Bovie (*J. Am. Med. Assoc.*, 1915-16, 33, 295). They also stated that the first hydrogen is neutralised at pH=3.5 and the second at pH=7.5 : the third did not exist in the solutions used by them. Britton (*J. C. S.*, 1927, 614) measured the hydrogen electrode potentials of a dilute solution of phosphoric acid during its progressive neutralisation by about decinormal sodium hydroxide and utilised the data for the calculation of the three dissociation constants of the acid. He found the value of the third dissociation constant to be seven times greater than that obtained by Abbott and Bray

(*J. Amer. Chem. Soc.*, 1909, 31, 729) but in agreement with the value obtained by Prideaux (*loc. cit.*). Prideaux and Ward (*J. C. S.*, 1924, 125, 423) examined the variation in the values of k_2 and k_3 with a change in the ratio, equivalent of alkali to moles of acid, from the data of other investigators. Lugg (*J. Amer. Chem. Soc.*, 1931, 53, 2554) used the quinhydrone electrode for finding the first dissociation of phosphoric acid in salt solutions. Hahn and Klockmann (*Z. Physik. Chem.*, 1930, 151, 80; Cf. also Hahn, Frommer and Schulze, *ibid.*, 1928, 133, 390) showed mathematically that the failure to detect the third point of inflexion in the potentiometric titration of phosphoric acid is to be attributed to the unfavourable conditions of concentration. The third dissociation of phosphoric acid has been determined by Kugelmass (*Biochem. J.*, 1929, 23, 587), Sanfourche (*Comp. Rend.*, 1931, 192, 1925) and by Kolthoff (*Rec. trav. Chim.*, 1927, 46, 350). Recently Britton and Robinson (*Trans. Farad. Soc.*, 1932, 28, 537) have followed the titration of a solution of phosphoric acid with sodium hydroxide using the glass electrode but the details of the data obtained are not given. Their comment on a similar work of Morton (*Quart. J. Pharm.*, 1930, 3, 438) is that the latter obtained lower pK values.

(b) The pH of alkali phosphates and their mixtures has been determined on account of their action as buffers or hydron regulators. Friedenthal (*Z. Electrochemie.*, 1904, 10, 113) a pioneer in the work on this subject, prepared a useful set of standard solutions by mixing decinormal solutions of primary and secondary sodium phosphates. Subsequent investigators discarded the calorimetric method used by him in favour of the more accurate electrometric methods. Prideaux (*loc. cit.*) used the hydrogen electrode to measure the pH of decinormal solutions of alkali phosphates. These measurements have also been made by Ringer (*Chem. Weekblad.*, 1909, 6, 446; *ibid.*, 1910, 7, 203) for dilute solutions of sodium phosphates and by Clark and Lubs (*J. Biol. Chem.*, 1916, 25, 479) and Cohn (*J. Amer. Chem. Soc.*, 1927, 49, 173) for solutions of potassium phosphates. Biilmann, Klit and Swaetichin (*Biochem. J.*, 1928, 22, 845) used the quinhydrone, quino-quinhydrone and hydroquinone electrodes for the measurement of pH of solutions containing primary phosphates of sodium and potassium. More recent workers on the pH of buffers containing alkali phosphates are Jowett and Millet (*J. Amer. Chem. Soc.*, 1929, 51, 1004); Nims (*ibid.*, 1933, 55, 946; 1934, 56, 1110) and Guggenheim and Schindler (*J. Phys. Chem.*, 1934, 38, 533).

EXPERIMENTAL

The e. m. f. of the combination

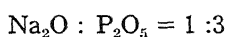
Pt.	Normal HCl saturated with quinhydrone	Glass membrane	Test Solution	KCl Saturated	KCl saturated calomel	Hg
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was measured by the method described in details by Mehta (this Journal, p. 77) in which Morton type glass electrode system is used in conjunction with Harrison's circuit improved upon by Greville and MacLagan with suitable modifications. The glass electrode was checked before and after each set of readings by means of the buffer solutions mentioned by Mehta (*loc. cit.*)

The solutions used in the investigation were prepared in the same manner as described in the previous communication (*loc. cit.*). The determination of the hydrogen ion concentration was made at 30°C.

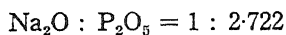
The results obtained are given in tables 1 to 6 in which N = Concentration of the solution in normality of its sodium content ; E = Observed e. m. f. of the concentration chain in volts.

TABLE I.



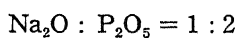
N	E	pH	H x 10 ¹
2	0.4238	0.495	319.9
1.5	0.4008	0.878	132.4
1	0.3951	0.973	106.4
0.5	0.3663	1.453	35.24
0.2	0.3383	1.920	12.02
0.1	0.3288	2.075	8.414
0.05	0.3154	2.301	5.00
0.02	0.3126	2.348	4.487
0.01	0.3046	2.481	3.304
0.005	0.2901	2.721	1.901

TABLE II.



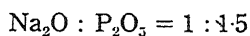
N	E	pH	H x 10 ⁴
2	0.4036	0.831	1476.0
1.5	0.3794	1.235	582.1
1	0.3633	1.503	314.1
0.5	0.3394	1.901	125.6
0.2	0.3173	2.270	53.7
0.1	0.3013	2.536	29.11
0.05	0.2943	2.651	22.34
0.02	0.2914	2.701	19.91
0.01	0.2753	2.970	10.72
0.005	0.2661	3.123	7.534

TABLE III.



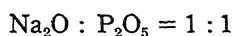
N	E	pH	H x 10 ⁴
2	0.3753	1.303	497.7
1	0.3456	1.798	159.2
0.5	0.3226	2.181	65.92
0.2	0.3029	2.511	30.83
0.1	0.2948	2.645	22.65
0.05	0.2833	2.836	14.59
0.02	0.2773	2.936	11.59
0.01	0.2705	3.050	8.913
0.005	0.2604	3.218	6.053

TABLE IV.



N	E	pH	H x 10 ⁴
2	0.3365	1.950	112.2
1.5	0.3283	2.086	82.04
1	0.3157	2.296	50.58
0.5	0.3043	2.486	32.66
0.2	0.2931	2.673	21.23
0.1	0.2865	2.783	15.48
0.05	0.2828	2.845	14.29
0.02	0.2726	3.015	9.661
0.01	0.2652	3.138	7.278
0.005	0.2595	3.233	5.848

TABLE V.



N	E	pH	H x 10 ⁴
2	0.3003	2.553	27.99
1.5	0.2903	2.720	19.05
1	0.2838	2.828	14.86
0.5	0.2748	2.978	10.52
0.2	0.2703	3.053	8.851
0.1	0.2669	3.110	7.762
0.05	0.2653	3.136	7.311
0.02	0.2569	3.276	5.297
0.01	0.2431	3.506	3.119
0.005	0.2320	3.691	2.037

TABLE VI.
 $\text{Na}_2\text{O} : \text{P}_2\text{O}_5 = 15 : 1$

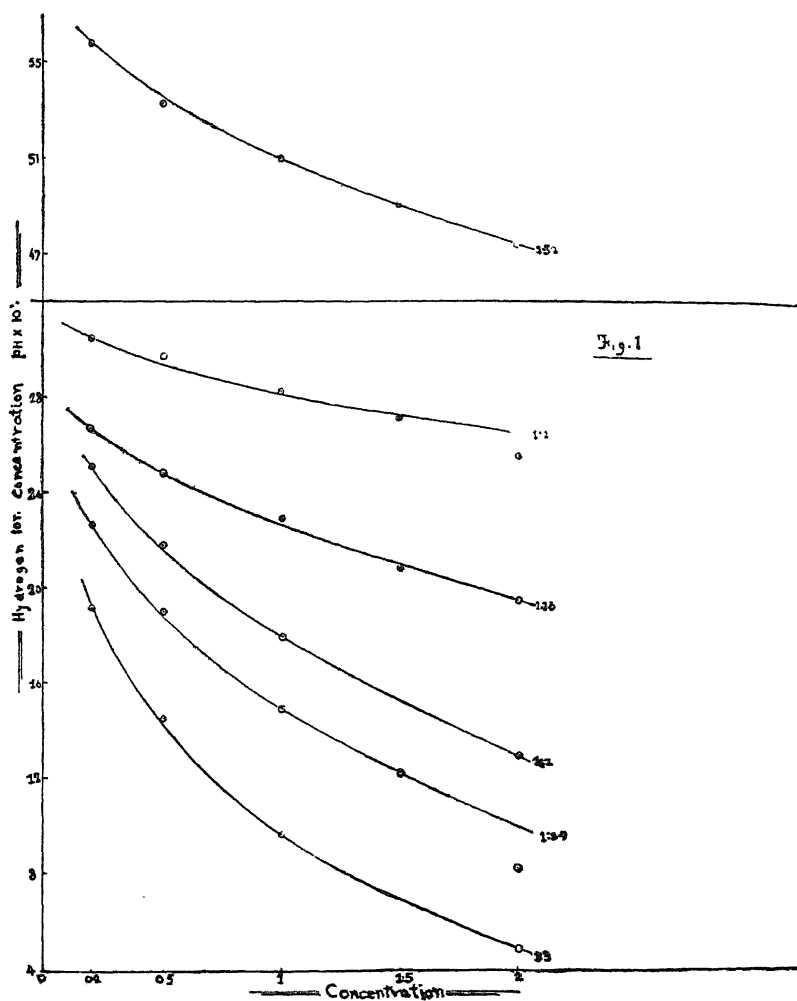
N	E	pH	N	Extrapolated pH	H (of Ex. pH) X 10^7
3	0.1848	4.47	2	4.74	721.0
2.25	0.1745	4.65	1.5	4.91	707.6
1.5	0.1582	4.92	1	5.1	83.91
0.75	0.1408	5.21	0.5	5.33	82.28
0.3	0.1252	5.47	0.2	5.585	80.75
0.15	0.1143	5.65	0.1	5.73	79.52
0.075	0.1062	5.78	0.05	5.85	78.89
0.03	0.0995	5.9	0.02	5.945	78.18
0.015	0.0958	5.96	0.01	5.98	77.96
0.0075	0.0944	5.985	0.005	6.01	9.02

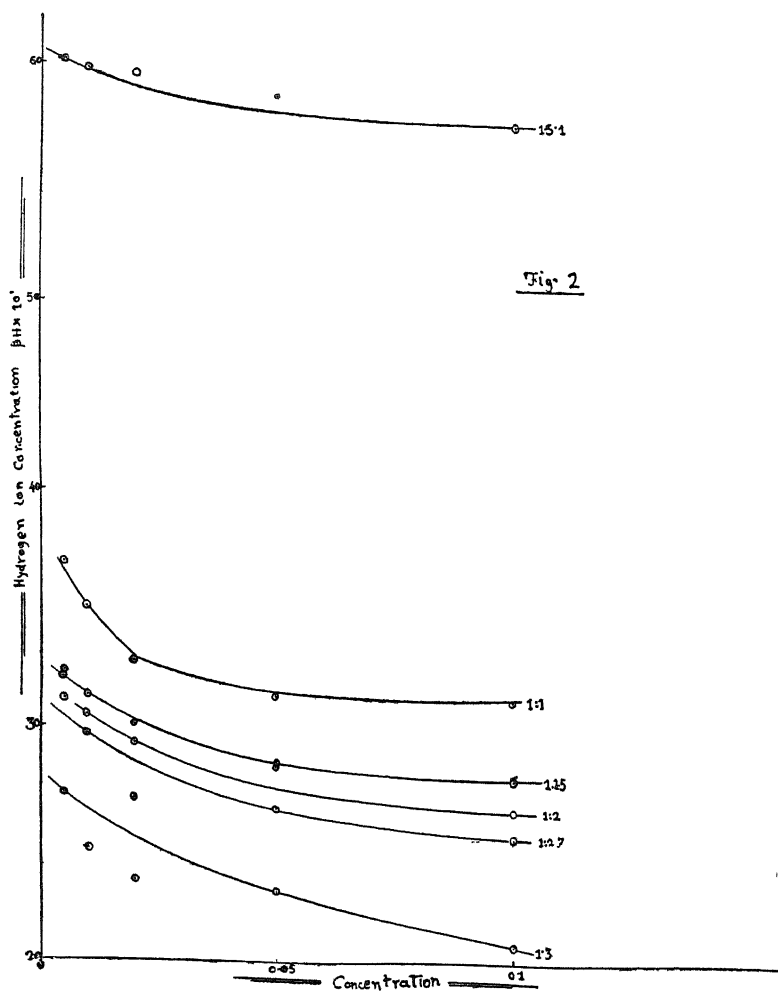
The pH values have been plotted against concentration and also against the ratio of Na_2O and P_2O_5 and the curves are shown in figures 1 to 3. Two sets of curves for concentrations from 2 N to 0.2 N and 0.1 N to 0.005 N are shown in figures 1 and 2. From these curves the values of pH corresponding to the different ratios of Na_2O and P_2O_5 (given in table 7) were obtained and the plot of these is shown in figure 3.

TABLE VII.

Ratios of $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$

N	1 : 3	1 : 2.7	1 : 2	1 : 1.5	1 : 1	1.5 : 1
2	0.49	1.02	1.31	1.95	2.65	4.74
1.5	0.71	1.24	1.54	2.1	2.72	4.91
1	0.98	1.5	1.7	2.27	2.81	5.1
0.5	1.43	1.9	2.17	2.49	2.94	5.33
0.2	1.93	2.29	2.51	2.69	3.05	5.585
0.1	2.075	2.54	2.64	2.78	3.11	5.73
0.05	2.31	2.65	2.73	2.84	3.13	5.85
0.02	2.53	2.86	2.94	3.03	3.29	5.945
0.01	2.65	2.97	3.05	3.15	3.5	5.98
0.005	2.72	3.04	3.12	3.21	3.69	6.01





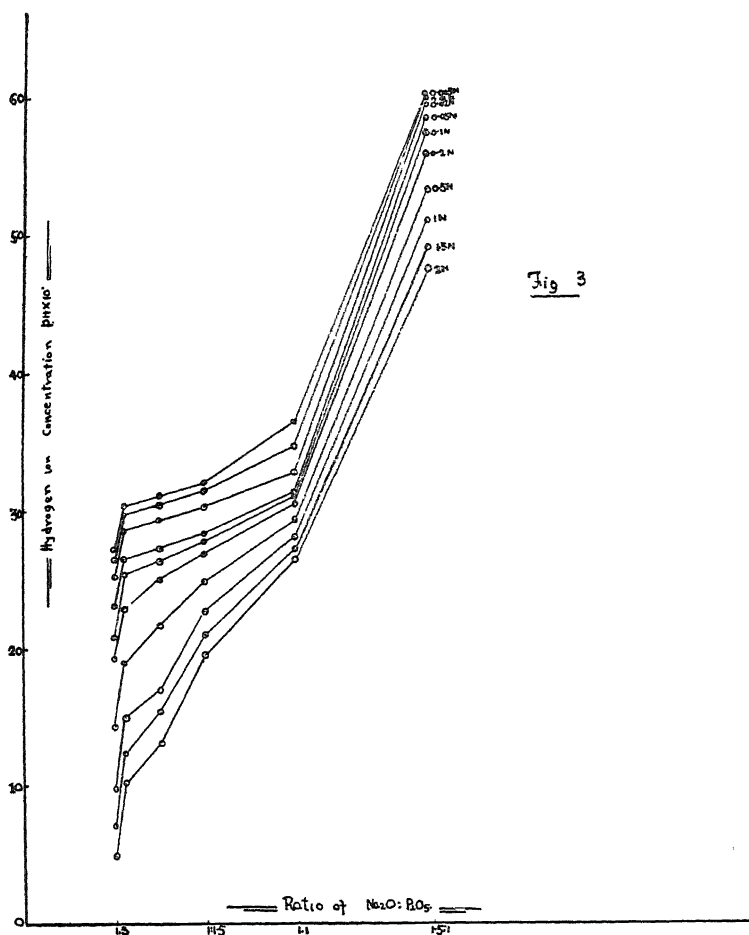


Fig 3

DISCUSSION

Considering first of all the effect of dilution it will be noticed from tables 1 to 6 and curves in figures 1 and 2 that the pH of all the solutions containing different ratios of Na_2O and P_2O_5 increases on dilution. Since $H = K_a \frac{1-\alpha}{\alpha}$ or $\text{pH} = \text{p}K_a + \log \frac{\alpha}{1-\alpha}$ where K_a = dissociation constant of the acid and α = degree of dissociation, an increase in the value of α will cause a decrease in $[\text{H}^+]$ or an increase in pH. It would appear from this that the observed increase in pH on dilution is to be attributed to an increase in the value of α . This is in agreement with what was stated previously (this Journal, p. 88) that the increase in the equivalent conductivity on dilution is due to an increase in ionisation.

The curves in figure 1 show that for concentrated solutions between 0.2N and 2N the variation in pH on dilution is more nearly linear with ratios 1.5 : 1 and 1 : 1 than with those containing higher proportions of P_2O_5 . Also in the latter this variation in pH is more rapid than in the former. In the case of dilute solutions (cf. figure 2) the pH varies slowly at first and then more rapidly as the dilution increases.

When the pH is plotted against the ratios of Na_2O and P_2O_5 , as was done for the data on equivalent conductivity (this Journal, p. 88), curves are obtained which are shown in figure 3. The similarity of these curves with the conductivity ratio curves in respect of the change of direction is at once discernible. The fall in pH is rapid as the ratio is changed from 1.5 : 1 to 1 : 1. At points corresponding to the ratio 1 : 1 there is a distinct change of direction, more pronounced than with equivalent conductivity ratio curves, and is due to the formation of the salt NaH_2PO_4 . As the relative amount of P_2O_5 is increased i.e. as the ratio $Na_2O : P_2O_5$ is decreased there is diminution in pH. But at points corresponding to the ratio 2 : 5 (approx.) there is a change of direction of the curves as in the case of the ratio 1 : 1. These points, therefore, may also indicate the formation of $2NaH_2PO_4 \cdot 3H_3PO_4$ in support of the postulate put forward in the previous communication (*loc. cit.*). There are two more changes of direction of the curves corresponding to the ratios 2 : 3 and 1 : 2 but they are distinct only in fairly concentrated solutions. In dilute ones they are hardly perceptible. These observations lend support to the existence of $2NaH_2PO_4 \cdot H_3PO_4$ and $NaH_2PO_4 \cdot H_7PO_4$ at least in concentrated solutions, as suggested before (*loc. cit.*)

One of the authors (S. M. M.) takes this opportunity to thank the University of Bombay for a grant from which part of the expenses on this investigation were defrayed.

Received 15th August, 1936.

A NOTE ON THE METHODS OF MEASURING SURFACE TENSION

By

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In a previous communication on this subject (*Bom. Univ. Journal*, 1935, 4 (2), 138) the values of surface tension given in column 2 of table II are inaccurate due to a mistake on the part of one of the authors (C. C. P.) while interpolating these values for concentrations given in column 1 of the table from the data of Livingston, Morgan and Schramm (*J. Amer. Chem. Soc.*, 1913, 35, 1848). When this mistake is rectified it is found that although the values for water and benzene are in good agreement with those of other investigators those for solutions of calcium chloride are much lower. This may be attributed, as done by Livingston, Morgan and Schramm (*loc. cit.*), to the fact that these solutions wet a glass surface with the greatest difficulty.

Received 15th August 1936.

EFFECT OF TEMPERATURE ON SOLUTIONS OF SODIUM PHOSPHATE IN THE PRESENCE OF ORGANIC ACIDS

By

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Mehta (*Proc. Acad. Sci., U.P.*, 1935, 5, 46-49) studied the effect of temperature on solutions of borax in the presence of polyhydric substances and several organic acids. A similar effect on solutions of sodium hydrogen phosphate in the presence of a number of organic acids has been observed and the results obtained are given in this paper.

The experimental method was the same as described by Mehta (*loc. cit.*) with this difference, however, that instead of using known amounts of the solid acids, their solutions in sodium phosphate were used. The substances used were benzoic, salicylic, succinic, oxalic, tartaric, citric, vanillic, phenyl-acetic, anisic and malic acids and acid sodium sulphate. These were Merck's extra pure chemicals and water free from carbon dioxide was used throughout.

Since the effect of temperature on all the solutions was similar, only a few representative results are given in tables I to III in which x represents c.cs. of the phosphate solution of concentration C added to a volume V of a solution containing Q gram. of the acid dissolved in 100 c.cs. of the phosphate solution to give a particular pink tint with phenolphthalein at temperature T .

TABLE I.
Salicylic acid.

Q = 0.2 g V = 4 c.c. C = 0.1 N		Q = 0.3 g V = 5 c.c. C = 0.15N		Q = 0.2 g V = 2 c.c. C = 0.2N	
T°	x	T°	x	T°	x
30	14.20	34	18.0	40	10.0
35	13.25	38	17.0	46	9.0
40	12.40	43	16.0	49	8.0
50	10.60	49	15.0	57	7.0
55	9.50	54.5	13.75	64	6.0
60	8.70	—	—	—	—

TABLE II.
Succinic acid.

Q = 0.2 g V = 2 c.c. C = 0.1N		Q = 0.4 g V = 1 c.c. C = 0.15N		Q = 0.2 g V = 2 c.c. C = 0.2N	
T°	x	T°	x	T°	x
25	22.70	33	18.0	35	23.0
30	21.42	41	16.0	41	21.0
35	20.10	46	15.0	45	19.0
40	19.0	51	14.0	48	17.0
45	17.60	56	13.0	54	15.0
50	16.20	—	—	—	—
55	15.0	—	—	—	—

TABLE III.
Citric acid.

Q = 0.6 g V = 1 c.c. C = 0.1N		Q = 0.4 g V = 4 c.c. C = 0.15N		Q = 0.2 g V = 2 c.c. C = 0.2N	
T°	x	T°	x	T°	x
30	20.95	40	20.0	38	20.0
35	20.30	51	19.0	44	18.0
40	19.30	58	18.5	48	16.0
45	18.50	62	18.0	57	14.0
50	17.65	69	17.0	65	12.0
55	16.90	—	—	71	10.0
60	16.07	—	—	—	—

The results show that the volume of sodium hydrogen phosphate required to give a standard tint decreases with rise of temperature and that the volume-temperature graph is a straight line just as it happens in the case of solutions investigated by Mehta (*loc. cit.*). This effect is caused by an increase in the hydrolysis of sodium phosphate and the sodium salt of the added acid. This conclusion is supported by the observation of Boidin (*Chem. Centr.*, 1904, ii, 1192; *Bull. Assoc. Chim. Suc. Dist.*, 1904, 22, 112) that the quantity of acid required for the neutralisation of sodium hydrogen phosphate increases as the temperature of the solution is raised.

Solutions of trisodium phosphate when examined in the manner described above did not show the same behaviour probably because it is hydrolysed almost completely into sodium hydroxide and sodium hydrogen phosphate (cf. Shields, *Phil. Mag.*, (5), 35, 365.)

One of the authors (N. M. S.) thanks Prof. R. L. Alimchandani for the facilities afforded for this work at the Karnatak College Chemical Laboratory.

Received 6th August, 1936.

PHENYL GLUTARIC ACIDS

PART I :— β - β -Di-Phenyl Glutaric acid

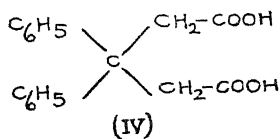
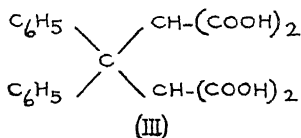
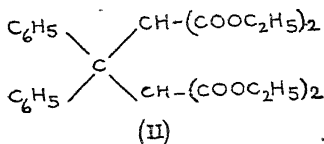
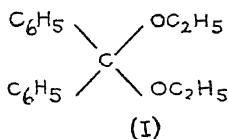
By

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Phenyl substituted glutaric acids are required in this laboratory in connection with the study of the rates of hydrolysis of anhydrides and imides of such acids. At present the following are known :— α -phenyl-glutaric acid [Fichter and Otto Merckens, *B.*, 1901, 34 4174] ; β -phenyl glutaric acid, [Michael, *J. Pr.* (2), 35, 352] ; α - β -diphenyl glutaric acid [Avery and McDole, *J.A.C.S.* 1908, 565] ; α α' di-phenyl glutaric acid, [Zelinsky and Feldmann, *B.* 22, 3290] ; $\alpha\beta\alpha'$ -tri-phenyl-glutaric acid [Henze, *B.*, 1898, 31, 3059]. The present paper describes the synthesis of β - β -diphenyl glutaric acid.

The Guareschi method (*Atti R. Acad. Sci. Iorino.* 1900-1901, 36, 443) as well as Thorpe's method (*J.*, 1919, 686) using benzophenone and cyanacetic ester or cyanactamide were not applicable. Similarly the Michael condensation of ethyl sodiomalonate with ethyl β -phenyl cinnamate did not take place. The condensation of benzophenone dichloride with ethyl sodiomalonate in presence of ethylalcohol gave diethoxy diphenylmethane (I) (cf. McKenzie, *J.*, 1896, 985). The dichloride condensed readily with ethyl sodiomalonate in presence of benzene under pressure giving a good yield of (II). Its alkaline hydrolysis gave the tetracarboxylic acid (III) which, on decarboxylation gave β - β -diphenyl glutaric acid (IV) which could also be obtained directly by hydrolysing the ester (II) with conc. hydrochloric acid. β - β -di-phenyl glutaric acid melts at 162°-163°. Some of its reactions and derivatives are described in the experimental part.



EXPERIMENTAL

Benzophenone chloride was prepared by the method of Kekule and Franchimont [*B.*, 1872, 5, 908). The first few attempts to prepare it were invariably failures. The cause was ultimately traced to rubber stoppers which should not be used in its preparation or distillation. It boiled at 235° at 70 m.m. and had the characteristic blue fluorescence.

Isolation of $\beta\beta$ diphenyl-propane $\alpha'\alpha'$ tetracarboxylic acid [III]:—To finely pulverised sodium (4.6g) suspended in dry benzene (100 cc.) was added ethyl malonate (32g.) and allowed to react for 12 hours with proper precaution against moisture. Benzophenone chloride [24g.] was then added. There was no reaction in the cold. This was then sealed in a pressure bottle and heated at 100°C for eight hours. It was cooled, acidified, and the benzene layer was separated, washed with a dilute solution of sodium carbonate, dried, and benzene removed, on water bath. The crude product [II] thus obtained weighed 45 grams. This was a dark-red viscous liquid which did not solidify when kept in vacuum and decomposed on distillation in vacuum [10 m.m.]. It was hydrolysed by heating it with excess of alcoholic caustic soda on water bath for six hours. The alcohol was then removed, the aqueous solution was extracted with ether to remove the unhydrolysed ester, and acidified, when a reddish gummy mass separated. This was then dissolved in dilute ammonia and excess of barium chloride was added. The precipitated barium salts were collected, washed, and decomposed by HCl. The solid thus obtained had a yellowish colour and melted at 110-120°C (with decomposition). It could not be obtained in a crystalline condition and did not give correct figures on analysis.

Isolation of β - β -diphenyl-glutaric acid [IV]:—The solid obtained as described above was heated at 140-150° for half an hour when decarboxylation had almost ceased. It was then treated with a dilute solution of sodium carbonate, boiled with the addition of animal charcoal, filtered, and acidified. The solid thus obtained was purified by recrystallisation from hot water. A better method of getting this compound is, however, to treat the crude condensation product [II] with concentrated HCl. The condensation product [II] (45g.) was boiled for 30 hours with conc. HCl (150 c.c.). At the end of this period the product had almost solidified. It was filtered, washed, treated with a dilute solution of sodium carbonate, boiled with the addition of animal charcoal, filtered, and acidified. The product thus obtained was purified by repeated crystallisation from boiling water. β - β -di-phenyl glutaric acid is insoluble in chloroform, benzene, and

petrol, slightly so in methyl, and ethyl alcohols, and fairly soluble in ethyl acetate. One part of it dissolves in 1500 parts of water at 30° and 220 parts of water at 100° . It separates from boiling water in shining colourless plates. M. P. $162-163^{\circ}$. [Found C, 72.20; H, 5.62 Equivt = 143.0. $C_{17}H_{16}O_4$ requires C, 71.83; H, 5.63 per cent. Equivt = 142]. Sodium, potassium, and ammonium salts are extremely soluble in water. Barium and calcium salts are somewhat soluble in water but cannot be crystallised from water. Lead and silver salts are insoluble. The silver salt prepared in the usual way was analysed. [Found Ag, 42.5 per cent. $C_{17}H_{14}O_4Ag_2$ requires Ag, 43.4 per cent.]

Methyl- β - β -diphenyl-glutarate :—The acid (5g.) was refluxed with methyl alcohol (25 c.c.) and con. H_2SO_4 (2.5 c.c.) for 3 hours. It was worked up in the usual way. It was a thick slightly coloured liquid and boiled at 210° at 30 m.m. N_D —1.55106 and $D_4^{31^{\circ}C}$ 1.13983.

Ethyl β - β -diphenyl glutarate :—The acid (10g.) absolute alcohol (50 c.c.) and con. H_2SO_4 (5 c.c.) were refluxed on water bath for 5 hours. The ethyl ester obtained (in 70 per. cent yield) was a thick liquid and boiled at $235^{\circ}C$ at 7 m.m. N_D = 1.53640 and $D_4^{31^{\circ}C}$ 1.09703. (Found C, 74.43; H, 7.02. $C_{21}H_{24}O_4$ requires C, 74.11; H, 7.06 per cent.).

β - β -diphenyl-glutaramide :—Methyl β - β -diphenyl glutarate (1 g.) and 50 c.c. of ammonia [density 0.88] were shaken together for two days. It was then diluted with water and the precipitated solid was filtered, and washed. It was soluble in the usual organic solvents. For analysis it was crystallised from hot water from which it separates in fine needles melting at 172° . The sample dried at 100° was analysed. [Found N, 9.60. $C_{17}H_{15}O_2N_2$ require N, 9.93 per cent.].

β - β -diphenyl-glutarimide :—It was prepared by the distillation of the ammonium salt and was purified by washing it with a mixture of benzene and petrol. Sparingly soluble in the organic solvents, it was soluble in dilute NaOH solution and melted at 188° . [Found N = 5.09 $C_{17}H_{15}O_2N$ requires N = 5.3 per cent.].

Di-anilide of β β -diphenyl glutaric acid :—This was prepared by the method of Douglas V. N. Hardy [J. C. S., 1936, 398]. Aniline [4 grams] was slowly dropped into a cold solution of ethyl magnesium bromide prepared from magnesium (1 g.) ethyl bromide (5 g.) and dry ether (30 c.c.). When the evolution of ethane had ceased methyl- β - β -diphenyl glutarate (3.2 g.) added. It was warmed on the water bath for 15 minutes. HCl was then added and extracted with ether. On removal of ether a black solid was obtained. On being crystallised from dilute alcohol, the di-anilide was obtained in the

form of pinkish needles. M.P. 185° . (Found N, 6.70. $C_{29}H_{26}O_2N_2$ requires N, 6.45 per cent.].

All attempts to prepare the anhydride have so far been unsuccessful.

We thank Dr. M. S. Shah for facilities.

(Received June 5, 1936.)

AN X-RAY INVESTIGATION OF THE CRYSTALS OF TRIPHENYLMETHANE

By

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1. Earlier Work.

The crystals of the stable modification of triphenylmethane have been examined crystallographically and have been found to develop the following faces :—

$$m \{110\}, a \{100\} \quad \text{and} \quad q \{011\}.$$

The crystals belong to the rhombic pyramidal class and the axial ratio is

$$a : b : c = 0.5716 : 1 : 0.5867.$$

(Groth, *Chemische Krystallg.*, V, 288)

Becker and Rose (*Zeit. Physik*, 14, 369-373 ; 17, 351, 1923 ; 24, 65-68, 1924) have studied the crystals by the powder method and have found that the number of molecules contained in the elementary crystal cell are four, the lengths of the axes being

$$a=14.52 \text{ A.U.}, \quad b=12.81 \text{ A.U.}, \quad c=7.42 \text{ A.U.},$$

and the axial ratio

$$a : b : c = 1.133 : 1 : 0.578.$$

Contrary to the conclusions of Becker and Rose, Mark and Weissenberg (*Zeit. Physik*, 17, 347-350, 1923) have found by the rotating crystal method, that the dimensions of the unit cell are

$$a=15.16 \text{ A.U.}, \quad b=26.25 \text{ A.U.}, \quad c=7.66 \text{ A.U.}$$

so that the axial ratio is

$$a : b : c = 0.5775 : 1 : 0.2918.$$

which agrees with Groth's ratio if the length of the *c*-axis is halved. Also the number of molecules per cell are eight and not four as found by Becker and Rose (*loc. cit.*).

2. CRYSTALS OF TRIPHENYLMETHANE.

Pure triphenylmethane from the 'British Drug House' was further purified by several recrystallisations from alcohol. Well developed crystals of the stable modification were obtained by a slow evaporation of a solution of the substance in alcohol. The melting point of the pure substance (a crystal was used for this purpose) was found to be 92°. The direction of the three crystallographic axes was found

out by measuring the various interfacial angles by mounting the crystal on the goniometric head of the 'Universal Photogoniometer' (Jour. Scientific Instrument, 6, 11, 343, 1929) and noting the reflections. The angles thus measured are given in Table I.

TABLE I.

Planes.	HINTZE a:c = 0.5716 : 0.5867		CALDERONS a:c = 0.5773 : 0.5806		BECKENKOFF a:c = 0.5786 : 0.5941		AUTHORS a:c 0.5719 : 0.2936
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
(100) : (110)	—	29°45'	—	—	—	—	30°0'
(011) : (0 $\bar{1}1$)	*60°48'	—	*60°17'	—	*61°34'	—	60°50'
(110) : (1 $\bar{1}0$)	*59°30'	—	*60°7'	—	*60°0'	—	59°48'
(021) : (010)	40°27'	40°27'	—	—	40°0'	40°5'	—
(110) : (011)	75°30'	75°27½'	74°24'	75°28'	75°10½'	75°10'	—
(021) : (110)	—	67°48½'	—	67°45'	67°29'	68°1'	—

NOTE :—The ratio a : c has been calculated from the observed angles marked with an asterisk (*).

3. EXPERIMENTAL RESULTS.

The crystals were investigated by the rotation and oscillation methods using x-rays from a Shearer gas tube fitted with a copper target. Rotation photographs (Plates I, II and III) taken about the three axes give the following dimensions for the unit cell :—

$$a=14.71 \text{ A.U.}, \quad b=25.72 \text{ A.U.}, \quad c=7.55 \text{ A.U.}$$

and the axial ratio

$$a : b : c = 0.5719 : 1 : 0.2936$$

which agrees very nearly with that obtained by Mark and Weissenberg (*loc. cit.*).

Oscillation photographs were taken about the three axes at intervals of 15° and the planes were indexed by means of Bernal's chart (*Proc. Roy. Soc., A*, 113, p. 117, 1926). The planes thus identified are given in Tables II and III in which is also given a comparative idea of the intensity of reflection as estimated by the eye (Robertson, 118, 712, 1928). The symbols used have the following meaning :

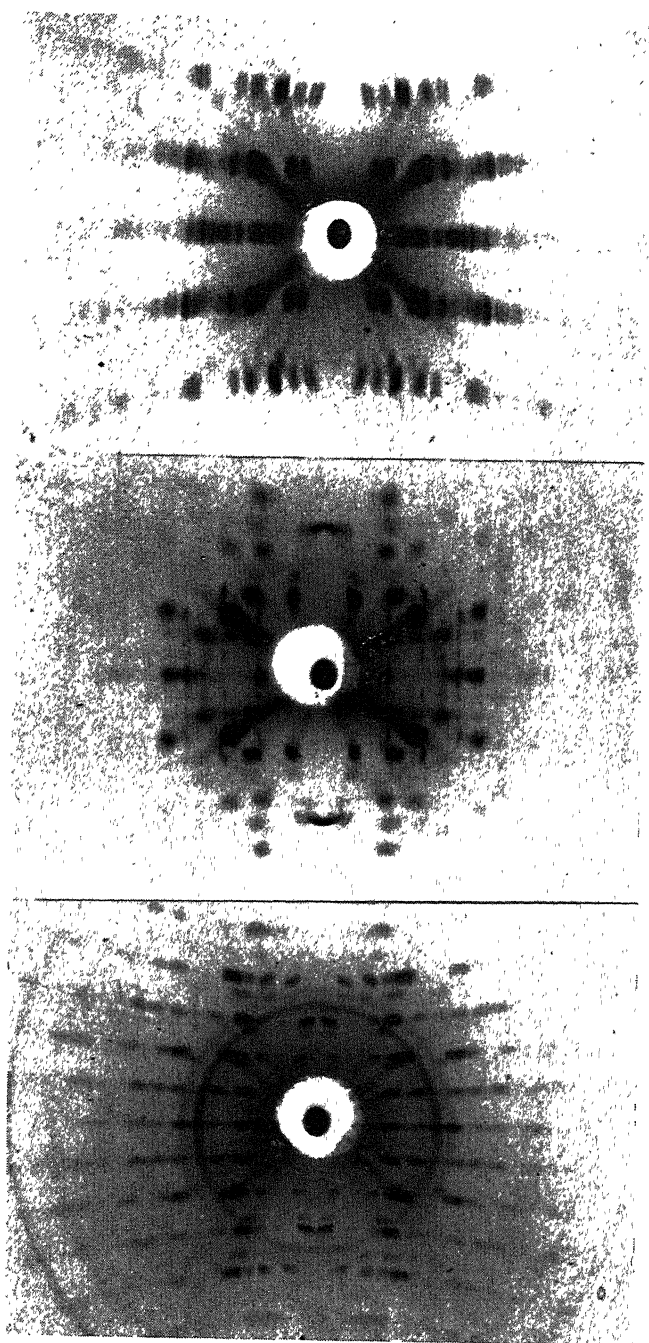
v.s.—Very strong
 s.—strong
 m.s.—medium strong
 m.—medium
 w.m.—weak medium
 w.—weak
 v.w.—very weak.

TABLE II.

AXIAL PLANES	PRISM PLANES				
	(okl)	(hol)	(hko)		
002 s	021 s	101 w.m	110 w	310 m	610 w
004 w	022 m.s	202 v.s	130 w	320 w.m	620 w
040 m.s	023 v.w	301 w	140 s	330 m	630 v.w
060 s	024 v.w	303 w	150 m	340 m.s	660 w
080 v.w	041 m	402 m	160 s	350 w.m	
0(10)0 w	042 w.m	501 w	170 m	360 w.m	720 w
0(14)0 v.w	043 w	602 w.m	190 w	370 w.m	750 w.m
200 v.s	061 m.s	701 w	1(10)0 w.m	3(10)0 w	
400 s	062 w		1(11)0 w.m	3(11)0 v.w	
600 m	063 w.m		1(12)0 w		
800 w.m	081 w		1(13)0 w	410 w	
	082 w		1(14)0 v.w	420 w	
	0(10)1 w		210 w.m	430 m.s	
			220 w	440 v.w	
			230 m.s	450 w.m	
			240 m	490 w	
			250 w.m	4(10)0 w.m	
			260 w	520 w.m	
			270 w	530 w.m	
			290 w	540 m	
			2(10)0 w	550 w.m	
			2(11)0 v.w	570 v.w	

TABLE III.
General Planes.

111 w.m	212 m.s	311 w.m	411 w.m	511 w.m	611 w
112 m.s	221 m.s	312 m	412 v.w	512 w	612 w.m
121 v.s	222 m.s	313 w	413 v.w	521 w.m	621 w
122 m.s	231 v.s	321 s	421 m	523 w	631 w
123 v.w	232 m.s	322 w.m	423 w.m	531 v.w	632 v.w
131 m	233 m	323 w	431 s	533 v.w	641 w
141 m.s	241 w	331 w.m	432 m	541 w.m	642 w
142 w.m	242 w	332 w.m	433 m	542 w	651 w
143 w	243 w	333 v.w	441 m	551 w.m	652 w
151 m	252 w.m	341 m	442 w.m	552 w.m	661 w
152 w.m	253 w	342 w.m	443 w	561 w.m	662 w
153 w.m	261 m	343 w	451 v.w	562 w.m	671 w
171 m	262 m	351 m	452 w	571 w.m	672 w
181 m	263 w	352 w.m	453 v.w	572 w	681 w
182 w.m	271 m	353 w	461 w	581 w	
183 w	272 w	361 w.m	462 w	582 v.w	
191 w.m	273 w	362 w.m	463 v.w	591 v.w	711 w.m
192 w	281 w	363 w	471 w	5(10)1 w	721 w
1(10)1 w.m	283 w	371 w.m	472 w	5(12)1 v.w	732 w
1(10)2 w.m	291 w	372 w	473 w		741 w.m
1(11)1 v.w	292 w	373 w	481 w		751 w
1(11)2 v.w	293 v.w	381 w	482 w		761 v.w
1(12)1 v.w	2(10)1 w	382 w	491 w		771 v.w
1(13)1 w	2(10)2 w	392 v.w	4(10)1 v.w		781 v.w
	2(11)1 w	3(10)1 w.m	4(10)2 w		
	2(11)2 w	3(10)2 w.m	4(11)1 v.w		
	2(12)1 v.w	3(11)1 v.w	4(11)2 v.w		
	2(13)1 v.w	3(11)2 w	4(12)1 w		
		3(12)1 v.w	4(13)1 v.w		
		3(12)2 v.w			
		3(13)1 v.w			



4. DISCUSSION.

The above tables show that (okl) planes are halved when k is odd and (hol) planes are halved when $(h+1)$ is odd. These halvings correspond to the space group C^9_{2v} if a and b are interchanged in Astbury and Yardley's tables (*Phil. Trans.*, A, 224, 221, 1924). The number of molecules required by the space group C^9_{2v} is four. This number can also be calculated from the dimensions of the unit cell and the specific gravity of the crystals (which was found to be 1.137) and was found to be eight (accurately 8.018).

The number of molecules is thus double of that required by the space group. Cases of this type, though rare, are known, for example, Caspari (*Phil. Mag.*, 1927, 4, 1276) found that the number of molecules in the unit cell calculated from the dimensions of the cell and the specific gravity of the crystals of some phenylene diamines is a multiple of the number required by the space group to which the abnormal halvings correspond. Such results can only be explained on the assumption that the asymmetric units are polymers of molecule and not single molecules themselves. Thus it appears that two molecules of triphenylmethane polymerise in some way to form one asymmetric unit of the elementary cell.

(Received August 25, 1936.)

CASHEW-NUT SHELL OIL AND A STUDY OF THE CHANGES PRODUCED IN THE OIL BY THE ACTION OF HEAT

By

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The pericarp of the cashew-nut, the fruit of the cashew-nut tree—"Anacardium occidentale" contains a reddish brown liquid commonly known as cashew-nut shell oil which is used on floors, wooden rafters, etc., to prevent the ravages of white ants. The oil is used also as a coating for boats and as a preservative for fishing nets. Its use for the manufacture of vermin proof, water proof and insulating varnishes has been developed recently by Dr. M. T. Harvey¹ of Irvington, N. J., U. S. America.

The oil which is produced only in India, is obtained as a by-product during the production of cashew kernels, and only a small portion of the oil is recovered. The export of cashew kernels mostly to U.S.A. from India is rapidly increasing due to the improved method of packing. The production of the cashew-nut shell oil has also consequently increased. The following table shows the export of cashew kernels from India to the U. S. A.

TABLE I.

Export of cashew kernels from India to the U.S.A.

Year	Amount of kernels in lbs.	Value in dollars
1930	3,880,257	813,151
1931	10,262,916	2,052,241
1932	9,722,300	1,602,281
1933	11,388,490	1,399,278
1934	14,610,467	2,308,320
1935	22,212,510	3,634,075

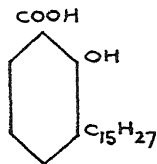
It is estimated that about 32,000 tons of raw cashew-nuts are roasted every year in India, and thus at the present rate of kernel

production nearly 13,000 tons of roasted shells containing nearly 18% oil are available, which could yield 53,000 gallons of the roasted nut shell oil. Almost all of these shells are at present wasted.

Cashew-nut shell oil was first investigated chemically by Stadelers² in 1847. He showed that cashew-nut shell oil was a mixture of an acid called by him anacardic acid and a non acidic substance cardol. He gave $C_{44}H_{32}O_5$ and $C_{42}H_{31}O_4$ as the molecular formulae for anacardic acid and cardol respectively. Ruhemann and Skinner³ established the formula $C_{22}H_{32}O_3$ for anacardic acid.

Anacardic acid has been further studied by Smit⁴ who confirmed the formula $C_{22}H_{32}O_3$ and showed that anacardic acid was an ortho-hydroxy-benzoic acid having a $C_{15}H_{27}$ side chain containing two double bonds. He hydrogenated anacardic acid to tetrahydro anacardic acid and also studied the decarboxylation of the acid.

Pillay⁵ has recently investigated anacardic acid. He has also hydrogenated anacardic acid to tetrahydro anacardic acid and studied the oxidation of its methyl ester. It may be mentioned that Pillay does not make any reference to the important work of Smit on the same subject. Both Pillay⁵ and Smit⁴ obtain palmitic acid on oxidation of the tetrahydro ester. Pillay has advanced the formula



for anacardic acid.

Cardol the other constituent has been mainly studied by Spiegel and Dobrin⁶, who prefer the formula $C_{32}H_{50}O_3$ for it. It appears to be a complex substance and no definite information is available on its chemical nature.

The present paper deals with a chemical study of the constituents and changes in the physical and chemical constants of the oil extracted from the shells of raw nuts on heating under different conditions. The study would be helpful in understanding the nature of the change undergone by the oil during the process of roasting of the nuts, and the properties of the oil in the roasted shells.

Another paper dealing with the drying properties of the cashew-nut shell oil from raw nuts as well as from roasted nuts, and also a study of the films of these oils formed on different types of surfaces, with a view to find the use of the oil in this country will be published elsewhere.

EXPERIMENTAL

The cashew-nuts were obtained from Malvan. The nuts were cut into halves and kernels were removed. The average weight of the nut was 4.5 gm., and on the average the ratio of weight of kernels to that of shells was 33 to 67.

Extraction of oil :—The raw shells were cut into small pieces about 0.2 cm. in breadth and were extracted with petroleum solvent, and also with rectified spirit in a Soxhlet apparatus. The petroleum solvent used was obtained by distilling ordinary motor petrol and collecting the fraction which distils over between 45° to 80°C. The petroleum solvent extracted all the oil in about 9-10 hours when it had syphoned down five to six times. Rectified spirit required 15-16 hours when it had syphoned down 14 to 15 times. The average yield of oil is about 33.5 per cent. of the weight of the shells, and about 22.5 per cent. of the weight of the nuts.

Physical and Chemical constants of Cashew-Nut Shell Oil :—It was found that samples of oils extracted from different batches of cashew-nuts showed an appreciable variation in their constants depending upon the locality of the nuts, age, degree of ripeness of the nuts and freshness of the nuts. The following table shows the constants of the oil extracted from different nuts :—

Constants.			Oil from fresh nuts.	Oil from first batch of nuts.	Oil from second batch of nuts.
Acid value	109	96	94
Saponification value	117	132	106
Iodine value	266	240	270
Specific gravity	0.9960	1.0026	0.9968

In order, therefore, to have uniform and representative results, nuts from one particular batch were used throughout this investigation.

The oil extracted from shells of fresh green nuts from the tree was light yellow in colour but it turned red brown after some time on keeping. The oil extracted from the commercial raw cashew-nut shells was red brown in colour. All attempts to decolorise the oil were unsuccessful.

The saponification value, acid value, iodine value, specific gravity, mean molecular weight, and acetyl value of the cashew-nut shell oil

extracted from the raw nut shells, and that from the factory discarded shells were determined.

Saponification value and acid value were determined by ordinary methods. Bromothymol blue Ph. 6 to 7.9 was used as an indicator instead of phenolphthalein to overcome the difficulty in marking the end point with the latter.

Iodine value :—Rosenmund and Kuhnemann's⁷ method was used after comparing its accuracy with Hanus's⁸ method. The former gave uniform results and took less time.

Molecular weight was determined by the freezing point method using benzene free from thiophene.

The following Table shows the authors' results as well as those obtained by previous workers :—

TABLE I.

The analytical constants of the cashew-nut shell oils.

Constants.	Extracted cashew-nut shell oil by Sudborough. ¹	Indian commercial oil by Sudborough. ¹¹	Indian commercial oil by Harvey.	Cashew-nut shell oil rendered in U.S.A. by Harvey.	Indian commercial oil by Crossly and Le'sure. ¹⁰	Extracted cashew-nut shell oil by the author.	Extracted cashew-nut shell oil from roasted shells by the author.
Acid value ...	107	18.8	19.5	36.5	...	94	nil
Saponification value.	119	32.9	38.5	66.7	44.5	106	4.5
Iodine value ...	296	328	265	294	267	270	294
Mean molecular weight.	470	340
Acetyl value	153	142	...	130	114
Refractive index	1.5163	1.5087
Specific gravity	1.0131 at 26°C	0.9623 at 26°C	0.972	0.984	0.9594 at 15.5°C	0.9268 at 25°C	0.9578 at 29°C

Distillation of shell oil under reduced pressure :—The oil from shells of raw nuts does not distil even under reduced pressure without undergoing decomposition. It distils over after decomposition between 250-280°C (10 mm.) and yields about 50 per cent. of a phenolic liquid which turns dark in colour after some time. The residue after distilling over of the light yellow phenolic liquid was a dark shining solid resembling asphalt. Only 75 per cent of this asphalt-like

material was soluble in benzene. The asphalt-like material when treated with benzene leaves behind a black solid mass. The benzene extracted material is a dark thick viscous liquid.

The phenolic light yellow liquid distillate was found to have the following constants :—

Specific gravity	0.8972
Acid value	72
Saponification value	13.0
Iodine value	185
Molecular weight	155

The light yellow phenolic liquid is insoluble in water and soluble in cold sodium hydroxide solution. It dissolves in concentrated sulphuric acid with evolution of heat to a deep red solution.

Separation and Estimation of Anacardic acid and Cardol :—
Anacardic acid and cardol were separated by an improved modifications of Stadeler's method.

The cashew-nut shell oil (2.3 g.) was dissolved in 95% alcohol (40-50 c.c.) and treated with an excess of freshly precipitated lead hydroxide suspended in alcohol. The mixture was boiled for $1\frac{1}{2}$ to 2 hours and kept at 3° to 5° over night. The precipitated lead anacardate was filtered and repeatedly washed free from the adhering cardol by alcohol, till a drop of the washed liquid did not show any turbidity with water.

Stadeler isolated anacardic acid from lead anacardate by treating the latter with ammonium sulphide, and treating ammonium anacardate thus formed with sulphuric acid. We found that anacardic acid is better obtained by treating a suspension of lead anacardate in water directly with hydrochloric acid. After heating for some time the anacardic acid floated on the surface. The solid cake formed on cooling was removed carefully and washed free from adhering acid by ice cold water. The acid adhering to the beaker was dissolved in chloroform and was added to the solid cake of the acid. The chloroform was evaporated off and the whole mass was dried at 95°C and weighed after keeping in a desiccator over calcium chloride.

The alcoholic solution after precipitation of anacardic acid contained cardol, and excess of lead hydroxide. The lead hydroxide was precipitated as lead sulphide by passing hydrogen sulphide. The alcoholic filtrate which now contained only cardol was light yellow in colour. Cardol recovered from the solution by evaporating the alcohol was a dark red oily liquid.

The following table shows the yield of anacardic acid and cardol from cashew-nut shell oil.

TABLE II.

Anacardic Acid and Cardol content of Raw Cashew-Nut Shell Oil.

Oil taken in grams	Acid obtained in grams.	Per cent acid	Cardol obtained in grams	Per cent cardol
2.6780	1.0915	40.6	1.5335	57.0
2.8895	1.1010	38.4	1.6900	58.0
1.0306	0.3970	38.5	0.5818	56.4
50.0	19.300	38.6	29.000	58.0

From the above table it will be seen that the oil consists roughly of 39% of anacardic acid and about 58% of cardol against 90% of anacardic acid and 10% of cardol reported by Stadeler and Pillay. On calculating from the results given by Smit ratio of acid to cardol is found to be 40 to 60.

The following table gives the constants of the acid and cardol :—

Constants.			Anacardic acid	Cardol.
Neutralisation value	158.8	20.2
Specific gravity at 29°C	1.007	0.9795
Iodine value	210	310
Molecular weight from neutralisation value	352.6	—
Molecular weight from cryoscopic method			355	488
Molecular weight from formula		...	344	500

Bromination :—The bromination of the cashew nut shell oil, anacardic acid, and cardol was carried out according to the method of Suzuki and Yakohama.¹¹

Bromination of the Oil :—About 2 to 5 grams of the oil was dissolved in 100 c.c. of the cold solvent and a cold solution of about 10 grams of bromine in 50 c.c. of the solvent was added slowly with constant stirring. The mixture was kept over night at 3° to 5°C. Next day the bromides were washed free from bromine. The solvent

was then evaporated, and the bromides weighed. The yields obtained are shown in the following table :—

Weight of the cashew-nut shell oil.	Solvent used.	Weight of bromides obtained.	Weight of bromides required by iodine value.	Weight of bromides per gram of oil.
5.1335 gms.	Petroleum ether	13.892 gms	13.890 gms.	2.707 gms.
1.1705 gms	Chloroform	3.168 gms.	3.162 gms.	2.707 gms
1.950 gms.	Carbontetra-chloride	5.277 gms.	5.265 gms.	2.700 gms.

Bromination of cardol :—About one gram of cardol was brominated in the same way as the oil. The bromo-compound was soluble in chloroform, carbon-tetrachloride, and benzene, insoluble in alcohol, and petroleum ether. 1.1064 gms. of cardol gave 3.158 grams of the bromo-product. Thus the bromine in the compound corresponds to 12 bromine atoms. The bromine was estimated by the Parr bomb method. The results are given below :—

Weight of bromide.	AgNO ₃ required by the bromide expressed as c.c. of 0.1 N AgNO ₃ .	Per cent of bromine in the bromide.	Per cent of bromine required for 12 bromine atoms.
0.1240 gm.	10.3 c.c.	66.3	65.7

The iodine value of the oil is 270. Calculating from the iodine value one gram of the oil should give 2.701 grams of the bromide. The oil is a mixture of 40% anacardic acid and 60% cardol. Anacardic acid absorbs 4 bromine atoms as shown by Pillay, and cardol absorbs 12 bromine atoms as mentioned above. On the above bases one gram of oil should give 2.524 grams of bromide, while on actual bromination one gram yields 2.700 to 2.707 grams of bromide. This difference is not clearly explainable at the present stage, but it may be due to traces of some other substance or due to some change produced by laccase which may be present in the oil. Smit reported that he obtained a light yellow viscous liquid which gets rapidly discoloured if laccase was added.

Bromination of roasted shell oil :—About 2 grams of the oil was brominated. The bromine in this compound corresponds to 8 atoms of bromine. 1.7952 gms. of the oil gave 5.156 gms. of the bromo-product.

Oxygen absorption :—As the oil has a high iodine value a series of experiments were performed to find out how much oxygen could be absorbed by the oil under certain conditions.

The oil was inserted into weighed U tubes containing pumic stone and dried oxygen gas was bubbled through the oil. The U tube was weighed at intervals to determine the increase in weight due to oxygen absorption. The experiment was repeated at higher temperatures keeping the U tube immersed in an oil bath kept at 200°C. Under this treatment also no increase in weight was observed but on the contrary it showed a slight decrease in weight. After heating for nearly four hours and bubbling oxygen gas at 200°C, the oil solidified completely to a dark mass, resistant to sulphuric, and chromic acids, sodium hydroxide and alcohol. From this it can be seen that the oil when heated at a higher temperature would give a resistant varnish. The drying of cashew-nut shell oil is, therefore, not due to oxygen absorption but due to condensation of the oil.

Effect of heat on cashew-nut shell oil.

The effect of heat on the physical and chemical constants of the cashew-nut shell oil was investigated by heating the oil in :—

- (a) air,
- (b) nitrogen,
- (c) sealed tubes.

Heating in air :—About 35 grams of the cashew-nut shell oil from raw nuts were heated in a two litre round bottomed flask (with a thermometer suspended in it) in an oil bath kept at a temperature about 5°C higher than the required temperature. The oil bath was first heated to the desired temperature and then the flask was inserted into it. The time of heating was marked after the cashew-nut shell oil had attained the desired temperature. The oil was heated at 100°, 120°, 150°, 175° and 200°C for $\frac{1}{2}$, 1, $1\frac{1}{2}$, 2, 3, 4, 5 and 6 hours.

About 40 grams of the oil was taken out each time after the required period and kept in well corked bottles. The constants of samples of the oil were then determined.

Heating in an atmosphere of nitrogen :—The oil was heated as above, the flask being closed by a rubber stopper with two glass tubes one leading purified nitrogen gas into the flask and the other serving for the exit of the gas.

Heating in sealed tubes :—The oil was heated in sealed Carius tubes, each of which contained about 40 grams of the cashew-nut shell oil. All tubes were in an oil bath kept at a temperature 5°C higher than the required temperature. After heating the tubes for

the required period, the tubes were allowed to cool and were opened next day.

All the results of the above determinations are given in the tables III, IV, V, VI, and VII, and are graphically represented in figs. 1, 2, 3, 4, 5, respectively. (See pp. 123—130).

The estimation of carbon dioxide evolved on heating the cashew-nut shell oil :—The amount of carbon dioxide evolved when the oil was heated at 100°, 125°, 150°, 175° and 200°C was estimated. The operation was carried out as follows :—

The oil was taken in a wide mouthed flask with a rubber stopper and heated in an oil bath at the required temperatures. The carbon dioxide was passed through an U tube containing sulphuric acid and then passed into the potash bulbs ; two series of bulbs were kept and alternately connected and disconnected by means of a two way cock in the middle. The amount of CO₂ evolved after different periods and at different temperatures was estimated. It was also estimated by using barium hydroxide and weighing the precipitated barium carbonate to make sure that the increase in weight of the potash bulbs was only due to the absorption of carbon dioxide and not due to the volatile phenolic compounds. The results of the carbon dioxide estimated by both methods agreed within the limits of experimental error.

Per cent of carbon dioxide evolved on heating the oil.

The following table shows the results obtained :

Temperature.	$\frac{1}{2}$ Hr.	1 Hr.	$\frac{1}{2}$ Hrs.	2 Hrs.	3 Hrs.	4 Hrs.	5 Hrs.	6 Hrs.
100°C	—	—	—	—	—	—	—	1.23
125°C	—	1.28	—	2.44	3.64	4.58	5.43	5.93
150°C	—	2.86	—	5.57	5.97	—	—	—
175°C	5.53	6.13	—	—	—	—	—	—
200°C	6.06	6.16	—	—	—	—	—	—

Theoretically raw cashew-nut shell oil can give 5.1 % of carbon dioxide, but when the oil is heated it will be seen from the above table that the maximum amount that could be obtained from the oil by heating it at 200°C comes to 6.16 per cent. The evolution of carbon dioxide can be mainly attributed to the decarboxylation of anacardic acid.

TABLE III.

Effect of heat on the saponification value of the cashew-nut shell oil

Temperature Deg- rees Centigrade.	Heated in.	SAPONIFICATION VALUE.								
		Pure extrac- ted Cashew- nut shell oil.	$\frac{1}{2}$ Hr.	1 Hr.	1 $\frac{1}{2}$ Hrs.	2 Hrs.	3 Hrs	4 Hrs.	5 Hrs.	6 Hrs.
100	Nitrogen	106	...	100	...	98	94	83	81	79
100	Air	106	...	100	...	97	95	90	85	84
100	Sealed tube	106	...	85	...	77	70	60	56	54
125	Nitrogen	106	91	85	...	67	57	37	22	15
125	Air	106	89	76	53	47	36	28	16	10
125	Sealed tube	106	74	70	45	40	28	16	10	7
150	Nitrogen	106	67	21	5	3	3	3	3	3
150	Air	106	72	48	17	9	6	5	4	4
150	Sealed tube	106	34	23	14	11	9	8	6	3
175	Nitrogen	106	5	5	4	3	3	3	3	3
175	Air	106	20	8	7	7	6	6	5	4
175	Sealed tube	106	24	21	16	16	10	10	7	6
200	Nitrogen	106	4	4	3	3	3	3	3	3
200	Air	106	6	6	5	5	5	4	4	4
200	Sealed tube	106	20	13	13	10	9	9	9	7

TABLE IV.

Effect of heat on the acid value of the cashew-nut shell oil.

Temperature Deg- rees Centigrade.	Heated in.	ACID VALUE.								
		Pure extrac- ted Cashew- nut shell oil.	$\frac{1}{2}$ Hr.	1 Hr.	1 $\frac{1}{2}$ Hrs.	2 Hrs.	3 Hrs.	4 Hrs.	5 Hrs.	6 Hrs.
100	Nitrogen	94	...	86	...	84	80	71	71	67
100	Air	94	...	87	...	85	84	79	75	74
100	Sealed tube	94	...	75	...	66	60	50	47	44
125	Nitrogen	94	81	74	...	56	45	28	14	7
125	Air	94	78	67	45	39	26	19	11	5
125	Sealed tube	94	65	63	40	35	23	11	5	3
150	Nitrogen	94	56	15	1	Nil	Nil	Nil	Nil	Nil
150	Air	94	64	41	11	3	1	Nil	Nil	Nil
150	Sealed tube	94	30	19	11	11	7	6	4	2
175	Nitrogen	94	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
175	Air	94	13	2	Nil	3	Nil	Nil	Nil	Nil
175	Sealed tube	94	18	16	11	11	6	5	3	2
200	Nitrogen	94	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
200	Air	94	1	Nil	Nil	Nil	Nil	Nil	Nil	Nil
200	Sealed tube	94	14	6	6	3	3	2	2	2

TABLE V.

Effect of heat on the iodine value of the cashew-nut shell oil

Temperature Deg- rees Centigrade.	Heated in.	IODINE VALUE.								
		Pure extrac- ted cashew- nut shell oil.	$\frac{1}{2}$ Hr.	1 Hr.	1½ Hrs.	2 Hrs.	3 Hrs.	4 Hrs.	5 Hrs.	6 Hrs.
100	Nitrogen	270	...	275	...	281	284	284	287	287
100	Air	270	...	274	...	276	281	281	282	282
100	Sealed tube	270	...	273	...	275	279	281	286	288
125	Nitrogen	270	278	280	...	284	292	297	308	309
125	Air	270	273	280	281	282	288	294	303	307
125	Sealed tube	270	273	276	283	288	291	297	300	307
150	Nitrogen	270	284	305	310	324	324	325	319	315
150	Air	270	278	287	302	310	319	315	314	310
150	Sealed tube	270	286	291	305	311	316	314	312	309
175	Nitrogen	270	315	318	317	316	314	312	312	310
175	Air	270	312	315	313	309	304	302	298	293
175	Sealed tube	270	310	311	309	308	306	303	300	296
200	Nitrogen	270	315	312	308	306	305	305	303	301
200	Air	270	310	308	305	303	299	296	290	288
200	Sealed tube	270	304	299	294	292	292	290	289	286

TABLE VI.

Effect of heat on the specific gravity of the cashew-nut shell oil.

Temperature Deg- rees Centigrade.	Heated in	SPECIFIC GRAVITY								
		Pure extract- ed Cashew- nut shell oil.	$\frac{1}{2}$ Hr.	1 Hr.	1½ Hrs	2 Hrs.	3 Hrs.	4 Hrs.	5 Hrs.	6 Hrs.
100	Nitrogen	0,9963	...	0,9943	...	0,9921	0,9900	0,9880	0,9860	0,9837
100	Air	0,9968	...	0,9944	...	0,9930	0,9914	0,9895	0,9869	0,9858
100	Sealed tube	0,9968	...	0,9854	...	0,9783	0,9753	0,9730	0,9707	0,9685
125	Nitrogen	0,9968	0,9915	0,9868	...	0,9775	0,9718	0,9641	0,9584	0,9554
125	Air	0,9968	0,9900	0,9822	0,9734	0,9703	0,9658	0,9629	0,9583	0,9568
125	Sealed tube	0,9968	0,9840	0,9807	0,9739	0,9714	0,9623	0,9562	0,9530	0,9525
150	Nitrogen	0,9968	0,9777	0,9581	0,9517	0,9508	0,9507	0,9508	0,9508	0,9508
150	Air	0,9968	0,9792	0,9682	0,9568	0,9543	0,9528	0,9522	0,9524	0,9525
150	Sealed tube	0,9968	0,9669	0,9640	...	0,9570	0,9551	0,9540	0,9525	0,9517
175	Nitrogen	0,9968	0,9501	0,9498	0,9498	0,9498	0,9498	0,9500	0,9502	0,9504
175	Air	0,9968	0,9572	0,9517	0,9507	0,9513	0,9577	0,9522	0,9526	0,9537
175	Sealed tube	0,9968	0,9588	0,9572	0,9551	0,9545	0,9535	0,9530	0,9513	0,9526
200	Nitrogen	0,9968	0,9491	0,9491	0,9494	0,9501	0,9506	0,9517	0,9527	0,9539
200	Air	0,9968	0,9509	0,9504	0,9505	0,9518	0,9520	0,9534	0,9565	0,9588
200	Sealed tube	0,9968	0,9575	0,9531	0,9532	0,9513	0,9519	0,9521	0,9535	0,9540

TABLE VII.

Effect of the heat on the mean molecular weight of the cashew-nut shell oil.

Temperature Deg- rees Centigrade.	Heated in.	MOLECULAR WEIGHT.								
		Pure extrac- ted Cashew- nut shell oil.	$\frac{1}{2}$ Hr.	1 Hr.	1½ Hrs.	2 Hrs.	3 Hrs.	4 Hrs.	5 Hrs.	6 Hrs.
100	Nitrogen	470	...	460	...	455	450	437	427	414
100	Air	470	...	458	...	456	443	438	422	410
100	Sealed tube	400	...	455	...	445	440	425	417	407
125	Nitrogen	470	435	420	...	415	395	377	362	344
125	Air	470	430	413	410	400	395	380	365	344
125	Sealed tube	470	427	405	400	400	401	395	372	351
150	Nitrogen	470	407	355	348	345	340	340	339	335
150	Air	470	400	357	350	342	345	336	334	330
150	Sealed tube	470	393	348	340	340	330	325	324	320
175	Nitrogen	470	342	328	335	335	338	345	349	354
175	Air	470	337	330	332	333	337	342	350	360
175	Sealed tube	470	341	330	334	339	344	350	358	363
200	Nitrogen	470	315	337	341	347	350	356	358	366
200	Air	470	318	330	340	349	358	359	371	380
200	Sealed tube	470	316	330	335	353	360	365	372	400

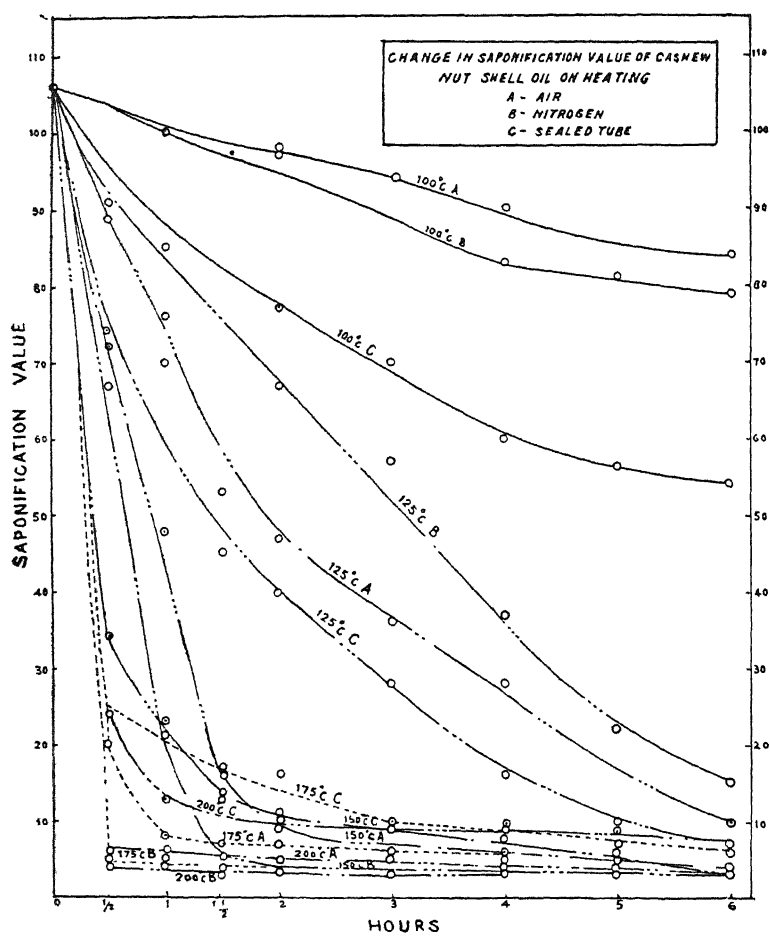


Fig. 3.

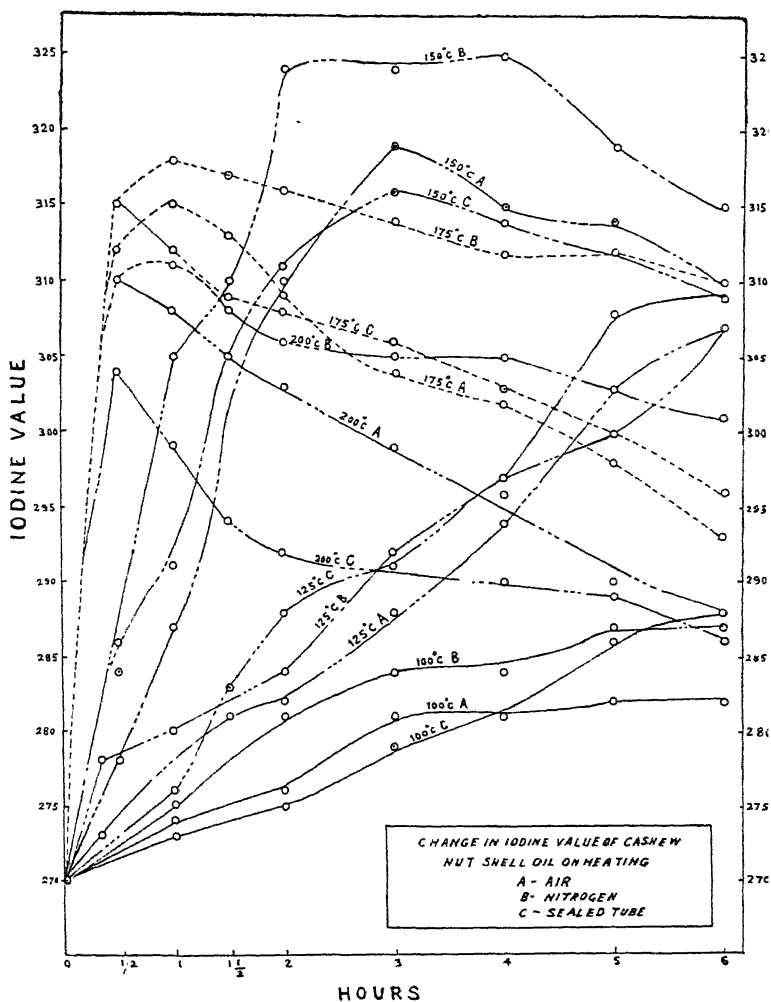
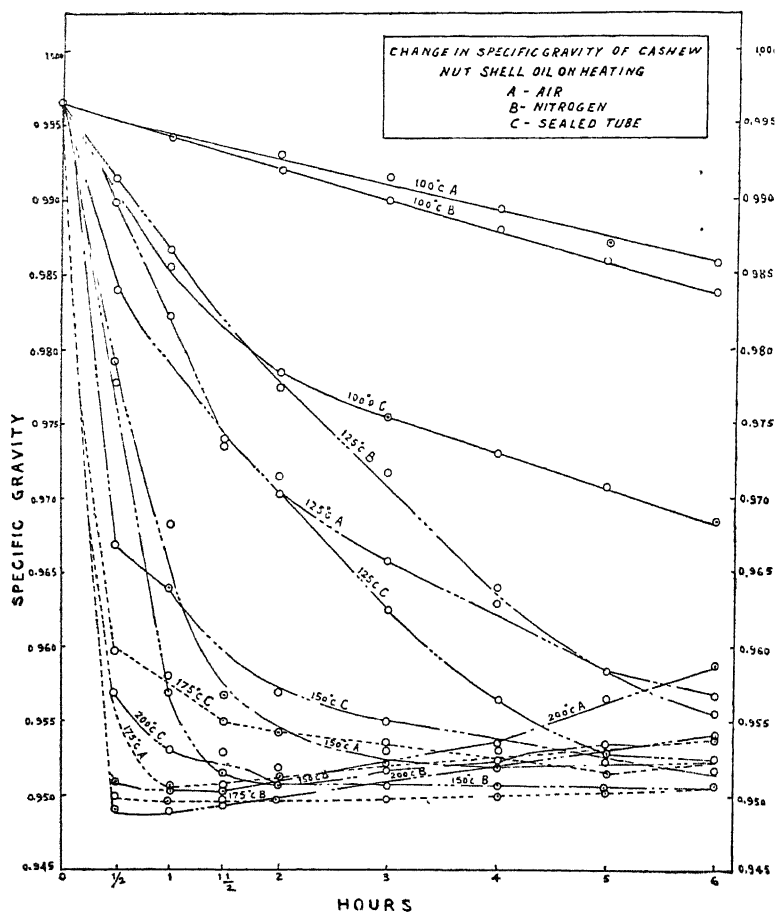


Fig. 4.



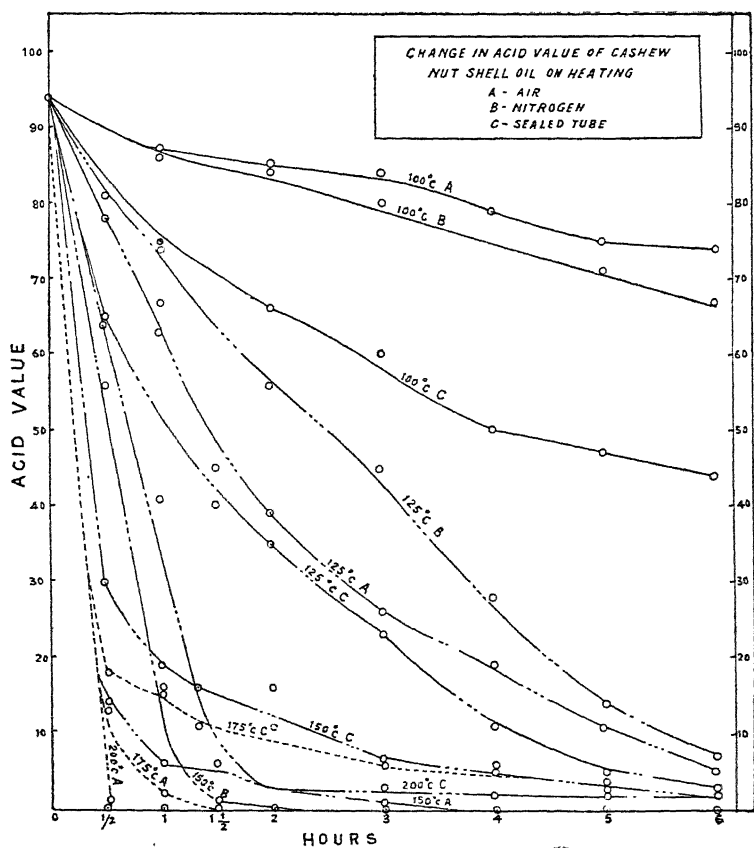


Fig. 2.

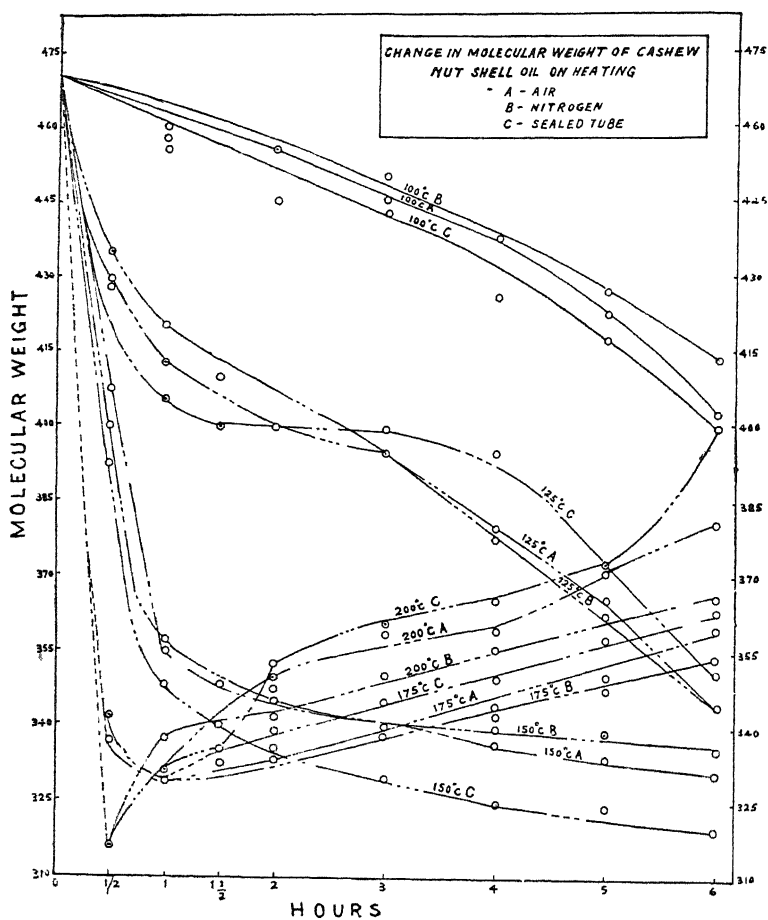


Fig. 5.

CONCLUSIONS

The saponification value and acid value of the oil decrease on heating until they become almost nil. The rate of decrease is higher at higher temperatures. This decrease is obviously mainly due to the decarboxylation of anacardic acid.

The initial increase in the iodine value on heating is partly due to the splitting off of carbon dioxide, and probably partly due to the decomposition of the oil into unsaturated substances. The subsequent decrease in the iodine value may be due to the condensation or polymerisation of the unsaturated decomposition products.

The specific gravity of the oil first decreases and then slightly increases on further heating. The mean molecular weight of the oil decreases to a minimum after which it again gradually increases.

All the above observations tend to show that the first stage in the change produced by heating cashew-nut shell oil from raw nuts is due mainly to decomposition of anacardic acid and probably to a small extent to the decomposition of the constituents of the oil, into substances of lower molecular weight. The subsequent stage in the change in the oil on further heating appears to consist of polymerisation or condensation or both.

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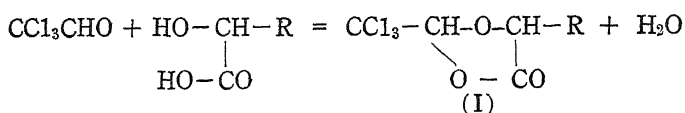
Received 25th August, 1936.

ISOMERISM IN CHLORALIDES--PART I.

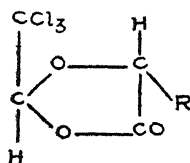
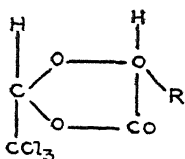
By

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The chloralides (I) formed by the condensation of chloral with α -hydroxy carboxylic acids, being saturated ring compounds, should exist in the *cis-trans* isomeric forms



according as the radicles, $-\text{CCl}_3$ and $-\text{R}$ are situated on the same side of the ring or on the opposite sides.



The work that has been published indicates that the chloralides have been only little studied with respect to stereo-isomerism. Of various chloralides in literature, only one form has been reported : Yorston, however, was able to get two products from the tartaric acid chloralide and suggested them to be *cis-trans* isomers (*Rec. trav. chim.* 1927, 46, 711).

The present authors during the course of their work on chloralides and their reduction products (*J. Indian C.S.*, 1934, 11, 535) prepared mandelic acid chloralide, the melting point of which differed from the one recorded by the previous workers, in spite of repeated crystallisations. The discrepancies in melting points that are to be found at present must needs be examined : some of them may prove to be due to the presence of *cis-trans*-isomers.

Workers on chloralides have not adopted a uniform method of preparation. This may lead to one form only being produced in any recognisable amount under the conditions of the experiment or the difference in the properties of the two forms may be too slight to admit of their separation. For the purposes of the present work, we

have prepared our chloralides, using H_2SO_4 as condensing agent, thus eliminating the first factor.

We have been able to separate two forms in the case of lactic, tartaric, racemic and mucic acid chloralides. Malic and citric acid chloralides could not be separated, indicating that possibly only one form is produced.

The following table gives the melting points of different forms of chloralides :—

Chloralide of	Shah and Alimchandani.	Previous Authors.
Lactic acid	(i) 56-57° and	45° or Wallach, (<i>Annalen</i> 1878, 193, 1).
	(ii) B. P. 212°	b.p. 212° Boeseken, (<i>Prod. K. Akad. Wetensch Amsterdam</i> , 1927, 30, 55-60). Bhatt and Meldrum, (<i>J. Uni. Bom.</i> , 1934, 3, 149).
Tartaric acid	(i) 161-162°	160° Yorston, (<i>loc. cit.</i>).
	(ii) 175°	173° " "
Racemic acid	(i) 161°*	122-124° Wallach., (<i>loc. cit.</i>).
	(ii) 213-215°	128-130° Bhat and Meldrum, (<i>loc. cit.</i>).
Mucic acid	(i) 175°	
	(ii) 198°	200-201° Bhat and Meldrum, (<i>loc. cit.</i>).

Lactic acid chloralide reported by the previous authors (*vide supra*) is evidently a mixture of two forms : (i) m.p. 56-57° and (ii) b. p. 212°. We have succeeded in isolating both the forms. Moreover, the substance b. p. 212° can be converted into one having m. p. 56-57° by heating above its boiling point. (cf. fumaric and maleic acid conversion). Tartaric acid chloralides have been already described by us (*J. Indian C. S.* 1934, 11, 535). Racemic acid chloralide has been stated by previous workers to melt at 128-130°. Our crude chloralide also melts at 125°. This product requires further working up for the separation of two forms, as described in experimental part. Evidently the substance of m. p. 125° or 128-130° (as described by the previous

* Racemic acid chloride of m.p. 161° is entirely different from the tartaric acid chloralide of m.p. 161-162°. The mixed melting point shows a considerable depression.

authors) is a mixture of two forms, (i) m.p. 161° and (ii) m.p. $213-215^{\circ}$. No previous worker has started with pure racemic acid, but their method of preparation involved racemisation. In the case of mucic acid chloralide, different forms are got depending upon the conditions for purifying the crude product : cold ether extraction gives one form, m.p. 198° , which is changed into the other, m.p. 175° by boiling with alcohol.

The *cis-trans* character of these substances is proved by (i) reduction by means of zinc dust and acetic acid, when the ring opens and the same reduction product is got (*J. Indian C. S.*, 1934, *11*, 535), (ii) by converting one form into the other by means of some suitable reaction.

EXPERIMENTAL

Lactic acid chloralide—Lactic acid (Merck, 1.16 : 41 g.) and chloral hydrate (45 g.) were mixed and conc. H_2SO_4 (45 c.c.) added slowly, the mixture being cooled under tap. The mixture was left overnight : it separated into two layers. The upper layer was removed, repeatedly washed with cold water when it partially solidified. The solid was filtered off and then crystallised from petroleum benzene, m.p. $56-57^{\circ}$: snow-white rectangular plates ; yield, 15 gms. It is soluble in all the common organic solvents. The substance has a camphor-like odour.

The oil which did not solidify was collected, dried over CaCl_2 and distilled : b.p. $210-212^{\circ}$. Yield, 12 gms. Even on keeping in a refrigerator, it does not solidify. (Found : Cl, 48.2 : $\text{C}_5\text{H}_3\text{O}_3\text{Cl}_3$ requires Cl, 48.5 per cent.)

The lower layer was poured into ice-cold water, when a small quantity of the chloralide was got, (Yield, 3 gms.) which was worked out as above.

If the oil (b. p. 212°) is heated above its boiling point, a distillate is obtained, which partially solidifies on keeping. This does not depress the melting point of the form, m.p. 56° , while the remaining oil boils at 210° . Possibly heating converts the *cis* form of the lower m.p. into *trans* form of the higher m.p.

Reduction of the lactic acid chloralides—Lactic acid chloralide (23 g.) was dissolved in glacial acetic acid (75 c.c.) and zinc dust (30 g.) was added in small instalments, the mixture shaken and cooled under tap, each instalment of zinc dust being added after the mixture attains the room temperature. It took about an hour for reduction and the mixture was then continuously shaken for about half an hour. It was filtered from unchanged zinc, diluted with water, neutralised with Na_2CO_3 , concentrated and a calcium salt prepared by adding

conc. CaCl_2 solution. On cooling, the calcium salt was filtered off and recrystallised from water (animal charcoal) : small needles. It crystallises with 2 molecules of water, of which one is removed by keeping in a desiccator or heating at 90° . (Found : Ca, 8.23 : $(\text{C}_5\text{H}_7\text{O}_3\text{Cl}_2)_2 \text{Ca} \cdot 2\text{H}_2\text{O}$ requires Ca, 8.3 per cent. After heating to constant weight at 90° , found : Ca, 9.11 : $(\text{C}_5\text{H}_7\text{O}_3\text{Cl}_2)_2 \text{Ca}$. H_2O requires Ca, 8.95 per cent.) The calcium salt was treated with dil. sulphuric acid : CaSO_4 removed and the oil that separated was extracted with ether, dried over anhydrous Na_2SO_4 and distilled., b. p. $218-220^\circ$. (Found : equivalent, 189.3 : Cl, 37.53 per cent. $\text{C}_5\text{H}_8\text{O}_3\text{Cl}_2$ requires equivalent, 187 : Cl, 37.94 per cent.)

Racemic acid chloralide—Racemic acid was prepared from tartaric acid according to the method given in 'Organic Synthesis, VI, page 82-83.' Instead of the metallic kettle as recommended therein, we have used a flask of suitable capacity with reflux condenser.

Racemic acid (15 g.), chloral hydrate (33 g.) and H_2SO_4 (50 c.c.) were mixed together and shaken for some time. After keeping overnight, the mixture was added to ice-cold water, when a solid separated which was collected, washed with cold water and dissolved in acetic acid : crystals were obtained, m.p., 125° . The melting points recorded in literature correspond to this substance (vide theoretical). On repeated crystallisations from a mixture of chloroform and petroleum benzene, two products could be separated : the form of m.p. 161° being in good quantity separated first as lustrous light needles, yield, 5 g., while the other of m.p. $213-215^\circ$ was got from the mother-liquor as dull white small crystals, yield, 4 g. (Found : Cl, 51.82 : $\text{C}_8\text{H}_4\text{O}_6\text{Cl}_6$ requires Cl, 52.03 per cent.).

Reduction of racemic acid chloralides—Racemic acid chloralide (10 g.) was dissolved in glacial acetic acid (30 cc.) and zinc dust (20 g.) added in small instalments as previously described. The reaction mixture was worked out as before and the reduction product separated as a calcium salt, which was recrystallised from water (animal charcoal). The calcium salt crystallises with 7 molecules of water which are removed on heating at $105-110^\circ$. (Found : Ca, 7.57 : $\text{C}_8\text{H}_8\text{O}_5\text{Cl}_4\text{Ca} \cdot 7\text{H}_2\text{O}$ requires Ca, 7.89 per cent. After heating to constant weight at $105-110^\circ$, found : Ca, 10.83 : $\text{C}_8\text{H}_8\text{O}_5\text{Cl}_4$, Ca, requires Ca, 10.5 per cent.

The acid was obtained from the calcium salt by treating with the calculated quantity of dil. H_2SO_4 : CaSO_4 was removed and the filtrate on concentration gave clusters of needles : yield : 3 g. Recrystallised from water and then from a mixture of ether and petroleum benzene, m.p. 158° . (Found : equivalent, 169.9 : Cl, 41.76 per cent. $\text{C}_8\text{H}_{10}\text{O}_6\text{Cl}_4$ requires equiv. 171.8 : Cl, 41.24 per cent.)

Mucic acid chloralide—Mucic acid (5 g.), chloral hydrate (12 g.) and H_2SO_4 (25 c.c.) were mixed. After three days, the mixture was poured over ice. The product was extracted with ether, small plates, m.p. 198° . The yield is not satisfactory as a good deal of the acid is recovered unchanged. (Found : Cl, 53.02 : $\text{C}_{12}\text{H}_7\text{O}_8\text{Cl}_9$ requires Cl, 53.34 per cent.)

If, however, the crude product is extracted with hot alcohol, the crystals melt at $174\text{--}175^\circ$. In spite of repeated crystallisations, the melting point did not rise.

To confirm the above, the pure chloralide of m.p. 198° was boiled with alcohol, when the crystals got melted at 174° . Thus boiling with alcohol brings about the transformation.

The work is being continued.

The authors are grateful to (the late) Dr. A. N. Meldrum for his interest in this work and to the University of Bombay for a grant to one of them (N.M.S.) which partially helped the investigation. We thank Mr. D. R. Kulkarni for his help in some of the experimental work.

Received August 25, 1936.

DERIVATIVES OF 1-HYDROXY-2-NAPHTHOIC ACID—
PART III.—ARYLAMIDES AND THEIR
BROMINATION PRODUCTS

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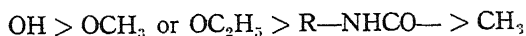
The present investigation is a study of the mode of distribution of bromine between the two nuclei of the arylamides of 1-hydroxy-2-naphthoic acid.

In the case of the anilide and the toluidides the action of one molecule of bromine gave 4-bromo derivatives, in which the bromine entered the para position to the -OH group in the naphthyl nucleus. The constitution of these were confirmed by establishing their identity by direct comparison with the arylamides obtained from 4-bromo-1-hydroxy-2-naphthoyl chloride (Derivatives of 1-hydroxy-2-naphthoic acid—Part I, Jadhav, Rao and Hirwe, under publication). When further brominated, these bromo-arylamides gave dibromo compounds, the additional bromine atom entering the phenyl nucleus, in the para position, except in the case of the p-toluidide where it entered the ortho position, the para being occupied. The constitutions of these compounds were confirmed by preparing them from 4-bromo-1-hydroxy-2-naphthoyl chloride and the respective bromoarylamines, prepared according to Cohen and Murray (*J.C. S.* 1915, 107, 848).

Bromination with one molecule of bromine of o- and p-anisidides and phenetidides of 1-hydroxy-2-naphthoic acid gave 4-bromo derivatives identical with those obtained from 4-bromo-1-hydroxy-2-naphthoyl chloride and the appropriate amine.

Further bromination of 4-bromo-1-hydroxy-2-naphth-p-aniside and p-phenetidide gave dibromo compounds, the bromine entering the position ortho to the alkyloxy group. 4-bromo-1-hydroxy-2-naphth-o-aniside and o-phenetidide gave on further bromination tribromo compounds, whose constitutions are under investigation.

These substitutions are in accordance with the usual order of the directing influences of the various groups as below :—



(cf. Holleman, *Rec. Trav. Chim.* 1923, 42, 360).

EXPERIMENTAL

1-Hydroxy-2-naphthanilide :—

A mixture of 1-hydroxy-2-naphthoyl chloride (Anschutz, Weber and Runkel, A. 1906, 346, 361) (from the hydroxy acid ; 5 g.), in dry benzene (40 c.c.) and freshly distilled aniline (6 g.) was kept at room temperature for an hour. The solvent was evaporated and the residue triturated with dilute HCl and the residual solid (4 g.) crystallised from acetic acid in white needles, m.p. 155-6°. (Anschutz, Weber and Runkel, *loc. cit.* ; m.p. 154°.).

4-Bromo-1-hydroxy-2-naphthanilide :—

A mixture of 1-hydroxy-2-naphthanilide (1 g.) in CHCl_3 (10 c.c.) and bromine (0.6 g.) in CHCl_3 (5 c.c.) was refluxed on a water bath for fifteen minutes. The solvent was evaporated and the residue crystallised from a mixture of acetone and rectified spirit in white needles, m.p. 164-5°. Mixed m.p. with 4-bromo-1-hydroxy-2-naphthanilide (Jadhav, Rao, Hirwe, *loc. cit.*) showed no depression.

4-Bromo-1-hydroxy-2-naphth-p-bromo-anilide :—

A mixture of 4-bromo anilide (2 g.) in hot acetic acid (20 c.c.) and bromine (1.2 g.), in acetic acid (10 c.c.) was refluxed on water bath when a crystalline solid (2 g.) slowly separated. It crystallised from acetic acid in wooly needles, m.p. 197-8°. (Found : N (micro) 3.4 ; Br, 38.0 ; $\text{C}_{17}\text{H}_{11}\text{O}_2\text{Br}_2\text{N}$ requires N, 3.3 ; Br, 38.0 per. cent.).

The same compound was also obtained from 4-bromo-1-hydroxy-2-naphthoyl chloride (from the bromo acid, 2 g.) and p-bromo-aniline (3 g. ; in 20 c.c. benzene).

1-Hydroxy-2-naphth-o-toluidide was prepared like the anilide (50% yield) ; crystallised from dilute rectified spirit, in white needles, m.p. 89-90°. (Found : N (micro), 5.4 ; $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}$ requires, N, 5.05 per. cent.) . ,

4-Bromo-1-hydroxy-2-naphth-o-toluidide was prepared like the anilide, using acetic acid and the solid obtained on dilution crystallised from rectified spirit in pinkish needles, m.p. 164-5°. Mixed m.p. with 4-bromo-o-toluidide (Jadhav, Rao and Hirwe, *loc. cit.*) showed no lowering.

4-Bromo-1-hydroxy-2-naphth-p-bromo-o-toluidide :—

It was prepared like the dibromo anilide, by refluxing the mixture on a water bath for an hour. The solid obtained (80%) crystallised from a mixture of dilute acetone and rectified spirit in small white needles, m.p. 177-8°. (Found : Br, 36.5 ; $\text{C}_{18}\text{H}_{13}\text{O}_2\text{Br}_2\text{N}$ requires Br, 36.8 per. cent.).

Mixed m.p. of the above product with the compound (m.p. $177-8^{\circ}$), obtained as above, from 4-bromo naphthoyl chloride and p-bromo-o-toluidine showed no depression.

1-Hydroxy-2-naphth-m-toluidide :—It was prepared like its o-isomer (40% yield). It crystallised from rectified spirit in pinkish needles, m.p. $118-9^{\circ}$. (Found : N (micro), 5.3 ; $C_{18}H_{15}O_2N$ requires N, 5.05 per cent.).

4-Bromo-1-hydroxy-2-naphth-m-toluidide was prepared by brominating the m-toluidide in the same way as its o-isomer. It crystallised from acetic acid in grey needles m.p. $201-2^{\circ}$. Mixed m.p. with 4-bromo-1-hydroxy-2-naphth-m-toluidide (Jadhav, Rao and Hirwe, *loc. cit.*), showed no lowering.

4-Bromo-1-hydroxy-2-naphth-p-bromo-m-toluidide was prepared (1) by bromination of the 4-bromo-m-toluidide and (2) from 4-bromo-1-hydroxy-2-naphthoyl chloride and p-bromo-m-toluidine. It crystallised from acetic acid in small pinkish needles, m.p. $171-2^{\circ}$. (Found : Br, 36.9 ; $C_{18}H_{13}O_2NBr_2$ requires Br, 36.8 per cent.).

1-Hydroxy-2-naphth-p-toluidide (50% yield) crystallised from rectified spirit in pinkish needles, m.p. $155-6^{\circ}$. (Found : N, (micro), 5.2 ; $C_{18}H_{15}O_2N$ requires N, 5.05 per cent.).

4-Bromo-1-hydroxy-2-naphth-p-toluidide was obtained on bromination of the foregoing compound crystallised from rectified spirit in pinkish needles, m.p. $148-9^{\circ}$. Mixed m.p. with 4-bromo-1-hydroxy-2-naphth-p-toluidide (Jadhav, Rao and Hirwe, *loc. cit.*) showed no depression.

4-Bromo-1-hydroxy-2-naphth-o-bromo-p-toluidide was prepared by bromination by refluxing the mixture for half an hour on the water bath. The solid (65%) that separated crystallised from acetic acid in wooly needles, m.p. $212-13^{\circ}$. The mixed m.p. with the product (m.p. $213-14^{\circ}$) from 4-bromo-naphthoyl chloride and o-bromo-p-toluidine showed no depression. (Found : Br, 37.0 ; $C_{18}H_{13}O_2Br_2N$ requires Br, 36.8 per cent.).

1-Hydroxy-2-naphth-o-anisidide (40% yield) crystallised from acetic acid in white needles, m.p. $161-2^{\circ}$. (Found : N, (micro), 5.1 ; $C_{18}H_{15}O_3N$ requires N, 4.8 per cent.).

4-Bromo-1-hydroxy-2-naphth-o-anisidide was obtained by refluxing a mixture of the o-anisidide (1 g.) in $CHCl_3$ (10 c.c.) and bromine (0.6 g.) in $CHCl_3$ (5 c.c.) for fifteen minutes. The solid obtained on evaporating the solvent crystallised from acetic acid in white needles, m.p. $180-1^{\circ}$ and mixed m.p. with the product m.p. $179-80^{\circ}$ from 4-bromo-1-hydroxy-2-naphthoyl chloride (from the bromo acid ; 6 g.)

and o-anisidine (6 g.) in dry benzene (50 c.c.) yield, (5.5 g.) showed no depression. (Found : Br, 21.7 ; $C_{18}H_{14}O_3$ BrN, requires, Br, 21.5 per cent.).

4-Bromo-1-hydroxy-2-naphth-? : ?-dibromo-o-anisidine was obtained by refluxing 4-bromo-o-anisidine (1 g.) dissolved under reflux in acetic acid (15 c.c.), to which bromine (1 g.) in acetic acid (5 c.c.) was slowly added and the heating continued till a crystalline solid (1 g.) separated, which crystallised from benzene in white needles, m.p. 233-4°. (Found : Br, 45.3 ; $C_{18}H_{12}O_3Br_3N$ requires Br, 45.3 per cent.).

1-Hydroxy-2-naphth-p-anisidine was obtained in 50% yield and crystallised from rectified spirit in pinkish needles, m.p. 129-30° (Found : N, (micro), 5.2 ; $C_{18}H_{15}O_3N$ requires N, 4.8 per cent.).

4-Bromo-1-hydroxy-2-naphth-p-anisidine was prepared by adding bromine (0.7 g.) in acetic acid (2 c.c.) to the anisidine (1g.), in hot acetic acid (10 c.c.) and crystallising the separated solid from acetic acid in pinkish needles, m.p. 155-6°. Mixed m.p. with the product (m.p. 155-6°) obtained from 4-bromo-1-hydroxy-2-naphthoyl chloride and p-anisidine showed no lowering. (Found : Br, 21.6 ; $C_{18}H_{14}O_3$ BrN requires Br, 21.5 per cent.).

4-Bromo-1-hydroxy-2-naphth-m-bromo-p-anisidine was prepared by refluxing for half an hour on a water bath, a mixture of 4-bromo-p-anisidine (2 g.), in acetic acid (20 c.c.) and bromine (1.3 g.) in acetic acid (10 c.c.). The solid (2 g.) that separated on keeping crystallised from dilute acetone and rectified spirit in small white needles, m.p. 195-6°. Mixed m.p. with the product (m.p. 196-7°) from 4-bromo-1-hydroxy-2-naphthoyl chloride and m-bromo-p-anisidine showed no depression. (Found : Br, 35.7 ; $C_{18}H_{13}O_3Br_2N$ requires Br, 35.5 per cent.).

1-Hydroxy-2-naphth-o-phenetidine (60% yield) crystallised from acetic acid in white needles m.p. 141-2°. (Found : N, (micro), 4.8 ; $C_{19}H_{17}O_3N$ requires N, 4.6 per cent.).

4-Bromo-1-hydroxy-2-naphth-o-phenetidine obtained by both the methods as before crystallised from acetic acid in white needles, m.p. 190-1°. (Found : Br, 20.6 ; $C_{18}H_{16}O_3BrN$ requires Br, 20.7 per cent.).

4-Bromo-1-hydroxy-2-naphth-? : ? : dibromo-o-phenetidine was prepared by refluxing a mixture of 4-bromo-o-phenetidine (1 g.) dissolved in acetic acid (40 c.c.) and bromine (1 g.) in acetic acid (10 c.c.) till a crystalline solid (1.1 g.) separated. It crystallised from a mixture of light petroleum ether and benzene, in white needles, m.p.

227-8°. (Found : Br, 44.2 ; $C_{19}H_{14}O_3Br_3N$ requires Br, 44.1 per cent.).

1-Hydroxy-2-naphth-p-phenetide was prepared in 38% yield and crystallised from rectified spirit in pinkish needles, m.p. 154-5°. (Found : N (micro), 4.8 ; C (micro), 74.1 ; H (micro), 5.6 ; $C_{19}H_{17}O_3N$ requires N, 4.6 ; C, 74.3 ; H, 5.5 per cent.).

4-Bromo-1-hydroxy-2-naphth-p-phenetide was prepared in the same way as its ortho isomer and crystallised from acetic acid in white needles, m.p. 179-80°, and the constitution proved in the same way. (Found : Br, 20.7 ; $C_{19}H_{16}O_3BrN$ requires Br, 20.7 per cent.).

4-Bromo-1-hydroxy-2-naphth-m-bromo-p-phenetide was obtained by refluxing for half an hour, a mixture of 4-bromo-p-phenetide (1 g.) in acetic acid (10 cc.) and bromine (0.6 g.) in acetic acid (5 cc.) and the solid (1 g.) that separated on cooling, crystallised from benzene in white needles, m.p. 201-2°. This constitution is assigned by analogy with 4-bromo-1-hydroxy-2-naphth-m-bromo-p-aniside (described above). (Found : Br, 34.6 ; $C_{19}H_{15}O_3Br_2N$ requires Br, 34.4 per cent.).

The authors thank Dr. T. S. Wheeler for his lively interest in the work.

Received August 1, 1936.

THE MECHANISM OF THE PHOTO-REDUCTION OF FERRIC CHLORIDE DISSOLVED IN ALCOHOLS

By

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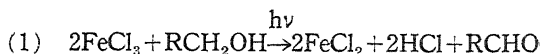
The photo-reduction of ferric salts in the presence of various organic compounds has been observed and studied by various workers (cf. Eder, *Sitzb. Wien. Akad.*, 1880, 82, 606 ; Ros, *J. Amer. Chem. Soc.*, 1906, 28, 790 ; Benrath, *Zeit. Physikal Chem.*, 1910, 74, 115 ; Winther and Oxholt-Howe, *Zeit. wiss. Phos.*, 1914, 74, 176 ; Pada and Miss Vita, *Gazetta*, 1924, 54, 147 ; Ghosh and Collaborators, *J. Indian Chem. Soc.*, 1929, 6, 827 ; 1932, 9, 237). The reduction of anhydrous ferric chloride by anhydrous methyl and ethyl alcohols in sunlight and the light from a quartz mercury vapour lamp was first observed and studied by Benrath (*J. Prakt. Chem.*, 1905, 72, 220 ; 1909, 80, 283 ; *loc. cit.*) and later by Prasad and collaborators (Prasad and Sohoni, *J. Indian Chem. Soc.*, 1931, 8, 489 ; Prasad and Limaye, *ibid.*, 1933, 10, 91 ; 1933, 10, 101).

Ferric salts have also been employed as sensitisers in photochemical reactions (cf. Neuberg, *Biochem. Zeit.*, 1910, 32, 209 ; Winther, *Zeit. wiss. Phos.*, 1908, 7, 66, 409 ; *ibid.*, 1910, 8, 125 ; Sanyal and Dhar, *Zeit. anorg. Chem.*, 1923, 128, 212). By studying the absorption spectra of several photo-sensitised mixtures containing the ferric salts, Winther (*Zeit. wiss. Phot.*, 1919, 7, 409 ; 1910, 8, 197 ; 1911, 9, 205) and Mukherjee and Dhar (*J. Ind. Chem. Soc.*, 1928, 5, 411) have conclusively shown that the photo-sensitivity of these mixtures is entirely due to the presence of ferric salts in them as even small quantities of these salts are sufficient to shift the absorption band towards long wavelengths. The sensitising action of the iron salts is explained on the assumption that these salts are first reduced by the action of light and the subsequent changes are caused during the re-oxidation of the reduced iron salt. However no direct experiments have so far been made in support of this view.

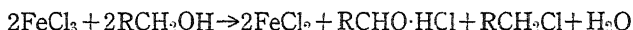
From the above explanation of the photo-sensitisation of ferric salt it may be inferred that the primary reaction in the photo-reduction of ferric chloride is the photo-decomposition of ferric chloride molecule. But it is also possible that the primary photo-chemical reaction involved in the reduction may be one of the following :—

- (1) $2\text{FeCl}_3 + \text{RCH}_2\text{OH} \xrightarrow{h\nu} 2\text{FeCl}_2 + 2\text{HCl} + \text{RCHO}$
- (2) $\text{FeCl}_3 \xrightarrow{h\nu} \text{FeCl}_2 + \text{Cl}$
- (3) $2\text{FeCl}_3 + \text{RCH}_2\text{OH} \xrightarrow{h\nu} \text{Complex} \rightarrow 2\text{FeCl}_2 + 2\text{HCl} + \text{RCHO}$
- (4) $\text{RCH}_2\text{OH} \xrightarrow{h\nu} \text{RCHO} + 2\text{H} \text{ or } \text{H}_2$
- (5) $\text{Fe}^{+++} \xrightarrow{h\nu} \text{Fe}^{++*} \text{ (activated).}$

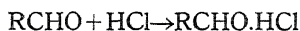
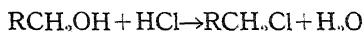
Hence in the following these possibilities have been examined and the results obtained have been used to elucidate the mechanism of the photo-reduction of ferric chloride in alcoholic solutions.



This view has been put forward by Benrath (*loc. cit.*). By exposing dilute solutions of ferric chloride in alcohols to artificial light and measuring the densities of the mixture at different intervals Benrath found that light does not act as a catalyst in these reactions. On analysing the reduced solutions he found that they contained hydrochloric acid, aldehyde, alkyl chloride and water and represented the complete reaction as



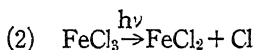
The formation of products other than those mentioned in the primary equation is caused, according to him, by the secondary reaction between alcohol and hydrochloric acid as



This mode of photochemical reaction suggests that the molecules of both ferric chloride and alcohol get activated by absorption of light and the collisions between these activated molecules result in the formation of the products. But this is impossible as alcohol does not absorb the white radiations and thus the alcohol molecules cannot directly get activated. The role which the alcohol molecules play in the photo-reduction of ferric chloride is, however, explained in the subsequent pages of the paper.

The possibility of Benrath's mechanism of the reduction of ferric chloride was examined by exposing in different flasks a solution of ferric chloride to which extra amounts of alcohol were added, to sunlight for the same interval of time. It was found that the reduction of ferric chloride decreases to a small extent with an increase in the

amount of the added alcohol and that there is no proportionality between the two. These observations confirm the view that alcohol does not take any direct part in the reduction of ferric chloride in the manner suggested by Benrath, for otherwise, the amount of reduction ought to increase instead of decreasing when the effective concentration of one of the constituents which also gets activated, is increased. These results are, however, in agreement with the conclusions that the rate of reduction is not independent of the concentration of ferric chloride and that it decreases as the concentration is decreased (cf. Prasad and Mohile, *National Acad. Sci.*, 1936, 6, 261).

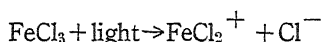


In order to examine this behaviour the action of sunlight on solid anhydrous ferric chloride was studied. In making these experiments all possible sources of contamination and errors were avoided. The apparatus used for the purpose consisted of three tubes connected with each other by stop-cocks. Pure dry ferric chloride was kept in one tube, phosphorous pentoxide in another and dry potassium iodide in the third. The whole apparatus was then exhausted and the pump-end of the apparatus was sealed off. The tap leading to the potassium iodide tube was then closed and the ferric chloride was allowed to stand for some time in darkness. When the stop-cock leading to the potassium iodide tube was opened no colour in the crystals was observed. The tube containing the ferric chloride was then exposed to sunlight and was shaken several times during exposure; the rest of the apparatus was shielded from light by covering it with black paper. After two days it was found that ferric chloride had turned greenish in colour suggesting that ferrous chloride had formed. The stop-cock leading to the potassium iodide tube was then opened and a definite coloration of iodine on the crystals of potassium iodide was noticed indicating the presence of chlorine in the tube containing ferric chloride. However, it is possible that ferric chloride which has a fairly high vapour pressure may volatilise and thus cause a liberation of iodine when passed over potassium iodide. The experiment was, therefore, repeated using a solution of potassium thiocyanate instead of potassium iodide to test the gas evolved. This only indicated the presence of ferric ions at the mouth of the tube containing ferric chloride. These experiments thus clearly show that ferric chloride gets reduced on exposure to sunlight without requiring the presence of an organic substance.

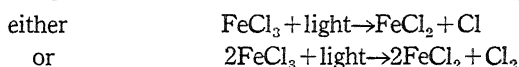
R. Audubert (*Jour. Chim. Phys.*, 1927, 24, 357) has also come to the same conclusion from his experiments on the measurement of photo-voltaic E.M.F. of the cell.



Hughes (Phil. Mag. 1912, 380) has shown that ferric chloride does not show any photo-electric effect and thus there is no possibility of ferric chloride decomposing into ionic chlorine as



The decomposition of ferric chloride, therefore, takes place as



If the decomposition of ferric chloride is the primary reaction taking place in the photo-reduction of ferric chloride in the presence of alcohols or other organic substances then it would be expected that the quantum efficiency is constant and equal to unity, irrespective of the concentration of ferric chloride, the wavelength of the light employed and the temperature, in accordance with Einstein's law of Photo-chemical Equivalence. But Winther and Oxholt-Howe (*loc. cit.*) have found that the quantum efficiency of the reduction of ferric chloride by organic substances changes considerably as the absorption coefficient of the solution is changed. Similarly Ghosh and Purukayastha (*loc. cit.*) have found that the quantum efficiency of the reduction of ferric chloride by organic acids varies considerably with wavelengths, being 1.36 for 399 $\mu\mu$ and 1.06 for 488 $\mu\mu$ in the case of mandelic acid. Prasad and Limaye (*loc. cit.*) have also recorded a similar variation of the quantum efficiency with the concentration of ferric chloride as well as with the wavelength of the incident radiation.

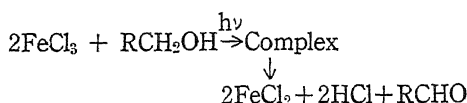
Also the temperature coefficients of the photo-reduction of alcoholic solutions of ferric chloride found by Prasad and Sohoni (*J. Indian Chem. Soc.*, 1931, 8, 489) in visible light and by the authors (cf. Table II) in the light from a quartz mercury lamp do not differ much from unity but are not exactly equal to unity.

TABLE II.
Solution in Ethyl Alcohol

Temp.	0.15 N.		0.23 N.	
	24°	10°	24°	10°
X x 10 ²	2.90	2.35	3.80	2.90
Temp. Coeff.	1.170		1.255	

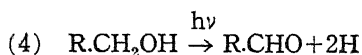
For this purpose the air inside the thermostat was cooled by means of a refrigerator at the top and was circulated inside the thermostat by a fan. The temperature was controlled by an automatic relay operated by the expansion or contraction of a hollow coil filled with air and was maintained constant to $\pm 0.2^\circ$.

Thus decomposition of ferric chloride by light in alcoholic solutions is evidently a process different from that found for the decomposition of pure ferric chloride. The improbability of this reaction being the primary one, is also shown by the fact that the accumulation of ferrous chloride in the reaction mixture does not seem to retard the reaction.



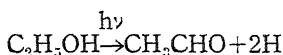
Winther (*loc. cit.*) has studied the application of the Beer's Absorption Law to solutions of ferric chloride containing organic acids and has concluded that there are several light absorbing compounds in these solutions. Ghosh and Mittra (*J. Indian Chem. Soc.*, 1928, 5, 191) have shown from the extinction coefficient measurements the formation of unstable intermediate compounds of ferric chloride and organic acid. Lloyd, Brown, Bonnell and Jones (*J. C. S.*, 664, 1928) have shown that ferric chloride combines with molecules of ethyl alcohol and forms an additive compound $\text{FeCl}_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$. It is possible, therefore, that an intermediate complex is formed in alcoholic solutions of ferric chloride when they are exposed to light and that this decomposes resulting in the reduction of ferric chloride. Thus two photochemical reactions will be going on side by side. A second possibility is that the complex is formed in the dark and it decomposes by the absorption of light. As yet no evidence is available in favour of the first possibility. As regards the second, the photochemical decomposition of the complex would be a reaction of the same type as discussed in (2) and would be open to the same objections as in the

case of the simpler mechanism $\text{FeCl}_3 \xrightarrow{h\nu} \text{FeCl}_2 + \text{Cl}$.

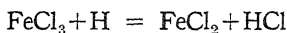


Burgoin (*J. Soc. Chem. Ind.*, 1923, 42, 574A) has shown that several reactions which are otherwise not possible can be made to take place in ultra-violet light (see also Berthelot and Gaudechon, *Compt. Rend.*, 1912, 154, 1597; 1912, 102, II 616). Henri and co-workers (*Comp. Rend.*, 1912, 154, 1261; 1911, 152, 535) have been able to decompose glycerol both pure and in aqueous solution into aldehyde etc. and have found that the reduction is hastened by the presence of

salts of iron, cobalt and uranium. Ethyl alcohol also decomposes in ultra-violet light with the formation of acetaldehyde and hydrogen (Berthelot and Gaudechon, *Compt. Rend.*, 1911, 153, 383) the aldehyde further decomposing into carbon monoxide and ethane. It is possible, therefore, that the primary process in the reaction is

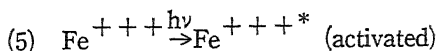


and takes place in the ultra-violet only. The nascent hydrogen thus generated would at once attack the ferric chloride and reduce it as



The formation of other products in the reaction mixture will take place as in (1). The ferric chloride in that case would play a double role in the photo-decomposition of the alcohol—primarily, that of an optical sensitiser by shifting the absorption of light by the solvent towards the longer wavelengths and secondly that of an acceptor of hydrogen generated by the decomposition of the alcohol.

In order to distinguish whether the reduction of ferric chloride in alcoholic solutions is brought about by the photo-reduction of ferric chloride or of the photo-oxidation of alcohol, the reduction of ferric chloride dissolved in benzene and toluene was studied. These solvents are chosen as they are themselves diactinic and are at the same time good acceptors of chlorine. Further, these solvents are non-polar and hence there is no possibility of any association taking place between the molecules of the solvents and those of the solute and also they will cause no dissociation of the ferric chloride. But even after a long exposure these solutions failed to show any measurable reduction. Thus no definite evidence for the primary photo-chemical reaction taking place in solution in alcohol could be obtained from these experiments. But when we consider the absorption of light by the reaction mixture, there remains little doubt that it is the ferric ions in the solution that are the principal recipients of the incident light energy and the hypothesis of the decomposition of alcohol being the primary photo-reaction in alcoholic solutions of ferric chloride does not stand valid. It is, however, possible that in the ultra-violet light which is absorbed by the alcohol, the decomposition of alcohol molecules may be going on alongside the reaction suggested later.



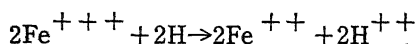
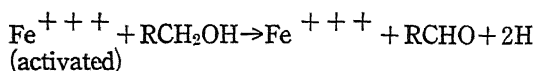
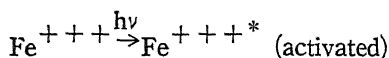
Allmand and Webb (*J. C.S.*, 1531, 1929) have studied the quantum efficiency in the photolysis of potassium ferri-oxalate by monochromatic light between the wavelength limits of 313-436 $\mu\mu$ and

have found it to be of the order of unity but decreasing with increase in wave-length. They have also found that for certain concentration limits the quantum efficiency is independent of the concentration of the photolyte. They have explained their results on the assumption that the primary result of the absorption of light is the activation of the ferri-oxalate ion which on collision with an unactivated ion gives rise to the products of photolysis. They prefer the mechanism of the activation of ions to the dissociation of the ferri-oxalate ion as the accumulation of ferrous oxalate does not retard the photolysis.

The photo reduction of ferric chloride in alcoholic solutions is a reaction similar to the photolysis of ferri-oxalate ion. The parallelism between the two can be seen from the observed facts that (i) the quantum efficiency of the reduction is nearly unity and varies with the wave-length of the exciting radiations, the concentration of the solution and the temperature at which the reaction is studied and (ii) the accumulation of ferrous chloride does not retard the reaction as X-t curves are straight lines.

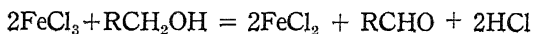
A plausible explanation of the observed results can thus be found if we suppose that by the absorption of a quantum of the incident light energy, the ferric ion or the ferric chloride molecule passes into a state containing surplus energy which it can impart to other atoms or molecules by colliding with them. If this energy is sufficient to produce a decomposition of the accepting molecules then only there is a likelihood of chemical change taking place, otherwise the molecule will revert to its stable state by emitting the extra energy in the form of either heat or fluorescence radiation. This may be taking place in the benzene experiments.

If it is supposed that some of the ferric chloride exists in the ionic state in alcoholic solutions (we are justified in making this supposition as Prasad and Limaye (*Loc. cit.*) have shown that these solutions are conducting) then it can be suggested that the energy is absorbed by the ferric ions, which consequently get activated, and is transferred to the alcohol molecules by collision. If this energy is sufficient to decompose the alcohol molecule a photo-chemical reaction should result. Thus,



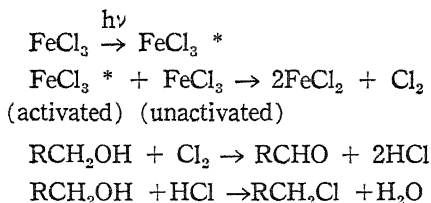
The net result of the process can still be represented by the equation

suggested by Benrath for the primary mechanism i.e.



The formation of other products will take place as explained under (1). The maximum photo-chemical efficiency, it will be seen, should on this hypothesis, be equal to two. Various values, less than 2 in all cases, some of which are greater than unity, have been obtained by various workers (*loc. cit.*).

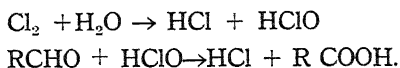
If, however, ferric chloride molecules get activated, then the mechanism of the reaction can be explained as follows :



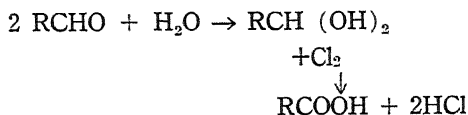
In this case also the quantum efficiency will be 2.

It may be possible to distinguish between the two mechanisms of activation if the energies of decomposition of the organic substances taking part in the reaction are known. But there is little doubt that this mode of consideration of the primary reaction taking place in alcoholic solutions of ferric chloride makes it possible to explain the observed variations in the quantum efficiency values with variations in the nature of alcohols, wave-lengths of the light source, temperature and other physical conditions. The formation of the complex, however, cannot be readily explained on this hypothesis unless the constitution of the complex is correctly known.

The photo-oxidation of the aldehyde observed by Benrath in the presence of aqueous solution of ferric chloride can also be explained from the above mechanism of the primary reaction in a simple manner as

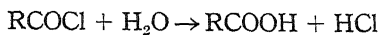
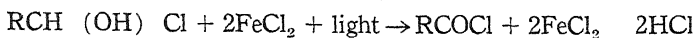
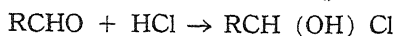
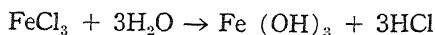


or as



The latter mode of reaction is supported by the experiments of Wieland (*Ber.*, 1912, 45, 2606). It may be mentioned here that Benrath

(*loc. cit.*) suggested the following mechanism



It is rather strange in the above mechanism that the reducing agents like formaldehyde and acetaldehyde do not reduce ferric chloride directly even in the presence of light.

Received September 10, 1936.

PETROLOGY OF THE SALSETTE ISLAND, BOMBAY

By

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Group II.—(A) : Andesine Andesite ; Altered Granophyre ; Olivine Basalt ; Porphyritic Olivine Basalt ; Olivine Basalt Porphyry ; Amygdaloidal Olivine Basalt (Tuff) ; (B) : Dolerite ; Olivine Dolerite ; Ankaramite ; Oceanite.

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Appendix A : Collection of Chemical Analyses and Norms.

INTRODUCTION.

This paper deals with the petrology of the volcanic rocks occurring at different horizons in the island and belong to the Upper Cretaceous age. It covers an area of about 241 square miles and lies immediately north of the island of Bombay from which it is separated by the Bandra-Kurla creek. On account of the importance of the island of Bombay as a site of commercial and industrial centre much literature has been published pertaining to the geology of that island from the structural, petrographical and engineering point of view, but very little attention has been paid in the past to the petrography of the island under discussion. It was thus desirable to obtain a comprehensive knowledge of the systematic petrography of the area and with this end in view, various quarries and exposures have been carefully examined, photographed and a large number of rocks fairly representing the different parts of the island were collected, sliced and

analysed. Norm values were calculated and a Variation diagram drawn. Geological map prepared is appended herewith (Map—B.).

PREVIOUS LITERATURE.

The previous literature on the island of Salsette is very scanty. It is limited to the papers of quite a few authors and is only confined to the description of the general geology of the area. A detailed account of the outcrops of these rocks is given by Dr. H. J. Carter as early as 1863. Mr. K. A. K. Hallows has given an account of the rocks and mineral resources of the island, in a paper entitled—"Report on the Geology of the Island of Salsette, Bombay Presidency, Poona, (1922)". Later on Dr. M. S. Krishnan in 1929 described the true nature of a rock type from Kherodiwadi, Malad (19° - $12'$ N : 72° - $49'$ E)¹ in the island of Salsette. Prof. H. C. Das Gupta described a specimen from Dharawi (19° - $2'$ - $30''$: 72° - $51'$) Bombay Island, as "white trap" which on thin sectional examination reveals its rhyolitic to trachytic character. In addition to these two areas, Prof. K. K. Mathur and others have recently recorded similar acid differentiates from Utan, Dongri (19° - $16'$: 72° - $47'$), Madh (19° - $8'$ - $10''$: 72° - $47'$) and Manori in the Island of Salsette. Four new areas containing the acid differentiates were discovered in this island. They are :—(a) Felsites, Rhyolites and Perlites of Santacruz-Khar area, (b) Granophyric Trachytes of Kurla, (c) Altered Granophyres and Rhyolite Ash of Jogeshwari Caves area, and (d) Augite Granophyres of Marol Hills. As regards the occurrence of ultrabasic rocks in this island, it is interesting to point out that they were never being recorded previous to this paper. The rock types discovered are Oceanites, Ankara-mites, and Olivine rich Dolerites.

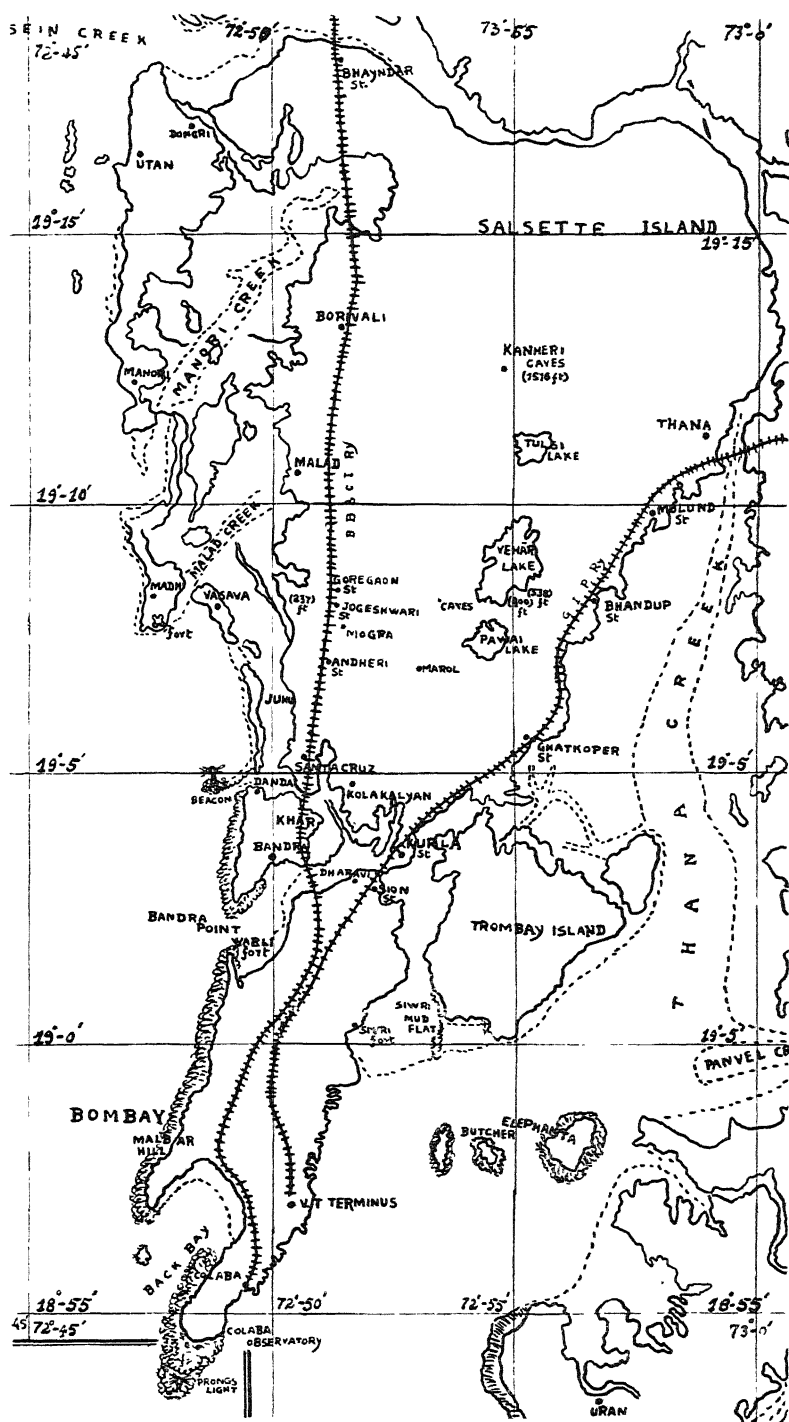
GENERAL FEATURES OF THE COUNTRY

Geographical. (Map—A)

The island of Salsette occupies a very prominent position on the coast-line of western India and lies immediately to the north of the island of Bombay. The general trend of the hills is north and south, with a gentle dip of 5° to 10° towards the north-west. The general aspect of the island can best be given by quoting the official report (Gazetteer of the Bombay Presidency., Vol. XIII Pt. ii (1882) pp. 685-6). "It is bounded on the north and north-east by Bassein or Thana Creek, on east by Bassein or Thana Creek, Kalyan and Panvel, on the south by Bombay harbour and on the west by the sea.

1 Elevations and place names in this paper have been taken from the latest one inch topographical sheets 47B|13 and 47A|16.

MAP—A



MAP OF SALSETTE AND BOMBAY ISLANDS

Along the centre of the island from north to south runs a broad range of hills, gradually falling southwards till it sinks into a plain near Kurla, and, after a break crops up again southern-most point of the island of Trombay. Towards the east along the foot of the hills, rough wood-lands are separated from the creeks and tidal swamps by a belt of rice land prettily wooded and well supplied with ponds. Spurs from the main range of central hills run west towards the sea from which they are separated by a wide plain broken by isolated hillocks. The low lands are much intersected by tidal creeks, which, especially on north-west, split the sea face of Salsette into many small islands".

Geological (Map—B).

Throughout the area the prevailing lavas are basalts of more or less uniform type, with occasional acid, intermediate, basic and ultrabasic intrusions together with pyroclastic ejecta. Further reference to the general geology may be taken from the previously quoted paper by Mr. K. A. K. Hallows.—

RECORD OF THE FORMER EXTENT OF THE DECCAN TRAP LAVAS.

Although at present day the Deccan Trap lavas cover an area of 200,000 square miles as remarked by W. T. Blandford, the former extent as observed by Wadia "could not have been much less than a million square miles". They cover areas of Cutch, Kathiawar, Gujarat, Deccan, Central India, Central Provinces, etc., with scattered outliers in Sind and in Rajahmundri on the east coast. With regard to their age, they are taken to be of the Upper Cretaceous or even younger than that corresponding to the earliest Eocene period.

EXTENT, DISTRIBUTION AND FIELD RELATIONS OF THE VARIOUS OUTCROPS OF IGNEOUS ROCKS STUDIED IN THIS AREA.

The distribution of the various rock-types and their field relations may be summarised as follows :—Basalts representing the plateau type constitute the major hill-masses and represent the first phase of extrusion. Dolerites with the characteristics of Deccan Trap basalts constitute rocks of minor intrusions and occur in the alluvial 'flats' of Kurla. One of the main dolerite intrusions forming a ridge ($19^{\circ} 8'N : 72^{\circ} 52'E$) traverses west of Jogeshwari railway station in a north-north-west south-south-east direction. The lava flows at Bandra Point, and extending upto Danda village ($19^{\circ} 4'-30'N : 72^{\circ} 30'$) are andesitic in nature and probably represent one of the phases of differentiation of the parental basaltic melt. The most prominent outcrops of the ultrabasic group occur in the neighbourhood of Vehar Lake (Figs. 15 and 16) where they form two hills—(538') and (400') ($19^{\circ} 8'-30' : 72^{\circ} 55'$). The area is only accessible by a petrol tram-

line owned by the Water Works Department, Bombay Municipality. Dykes of basaltic composition are associated with this ultrabasic mass. The commonest types are Oceanites, Ankaramites, and olivine rich Dolerites. The acid intrusions may be described comprehensively as Perlites, Felsites, Rhyolites, Granophyres, Trachytes and Augite-Granophyres. They exist into four areas namely—(1) Santacruz-Khar, (2) Kurla, (3) Jogeshwari, and (4) Marol. Briefly the intrusions of first two areas are narrow and hardly rise to a vertical height of 10 feet above the general level of the ground. The intrusions of the last two groups occur as vertical sided 'bosses' (this is especially true of Marol) and attain a maximum width of almost half a mile, and an height of about 150 to 200 feet. Moreover, there are important petrographical differences between these groups e.g. the rocks of Santacruz-Khar area are invariably rhyolitic, whereas those of Kurla and Marol are trachytic and often carry fresh augite. Rocks of Jogeshwari are granophyric in aspect and approach petrographically more to the rhyolites of Santacruz-Khar area than to the trachytes of Kurla and Marol. Chemically all the rocks belong to the suit characterised by excess of Soda over Potash.

Four new areas (where acid and intermediate rock types are discovered) are as follows :—

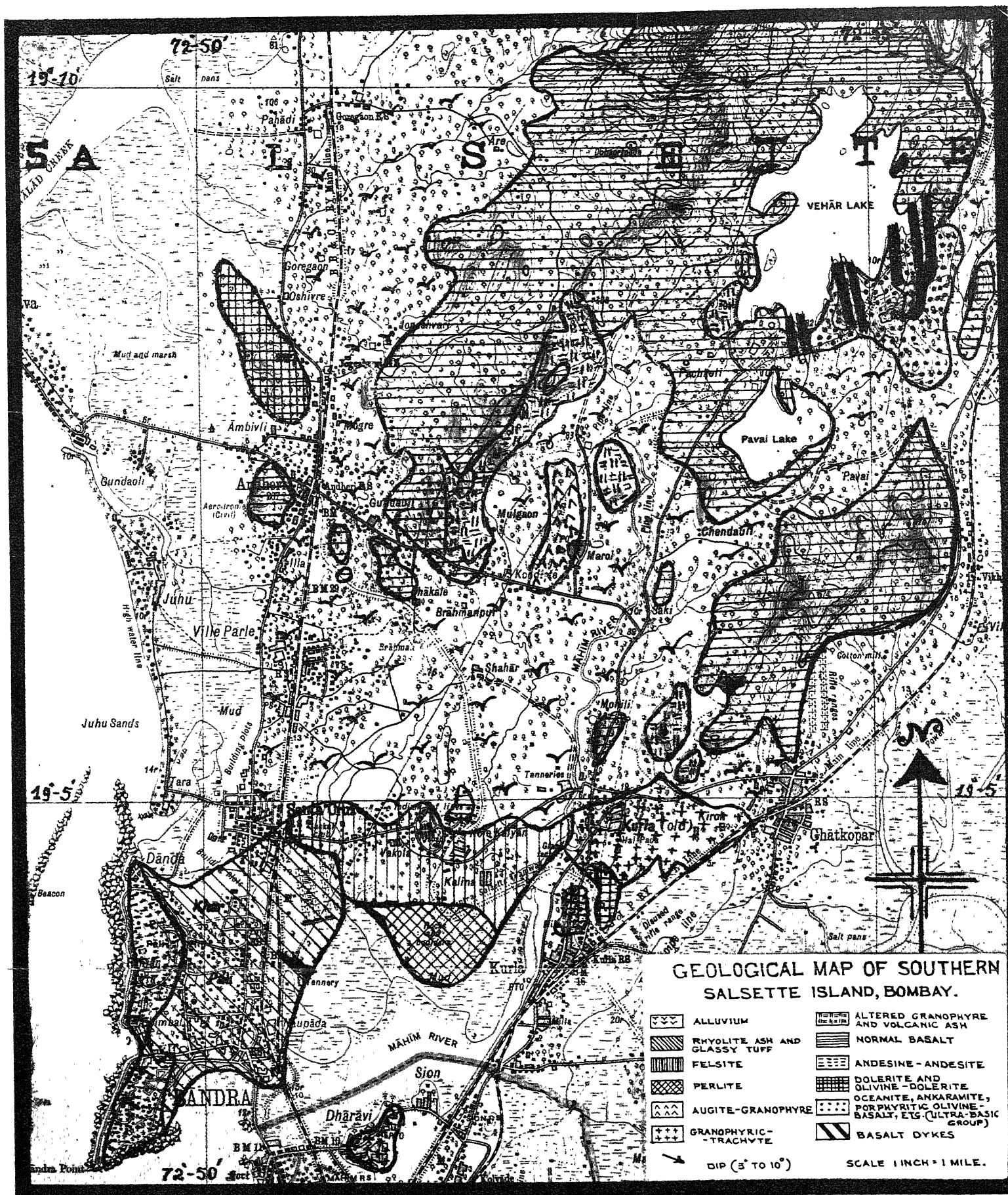
Area	Rocks Types
(A) Santacruz-Khar	Felsites (Fig. 4)
	Rhyolites (Fig. 5)
	Perlites (Fig. 3)
(B) Kurla	Granophyric Trachyte (Fig. 6)
(C) Jogeshwari Caves ..	Altered Granophyres (Fig. 2)
	and Rhyolite-ash (Tuff)
(D) Marol Hills	Augite Granophyre (Fig. 1)

A petrographic description with chemical analyses of these rock-types is already published by the authors in a paper entitled "The Occurrence of Some Acid and Intermediate Rock-Types in the Salsette Island, Bombay." *Quarterly Journal of the Geological, Mining and Metallurgical Society of India*, Vol. VII, No. 4, pp. 184-191 (1935).

ANDESINE ANDESITE

Locality :—This rock type is prevalent on the west coast of the islands of Bombay and Salsette. The rock under study is from a quarry near the village of Danda, (19°-4'-30" : 72°-40'-30"). Megascopically the rock is compact and blackish in colour. The broken edges are sharp with a conchoidal fracture. Under the microscope (Fig. 7) the rock shows a felted or andesitic texture and consists of

MAP-B



dark brown glass and lath shaped felspar microlites enclosing between them small but abundant subidiomorphic crystals and granules of augite. Iron ores are scattered throughout the dark brown glassy ground mass. Scaly variety of iron ores may be titaniferous—ilmenite. Olivine is extremely rare. However, a few pale greenish pseudomorphs probably leucitic in nature recall from the general outline and shape, the secondary origin from the parent olivine crystals. Felspar microlites of the groundmass give extinction angles varying from straight to 4° , indicating the oligoclase andesine variety. A few microphenocrysts are of andesine labradorite type. Augite is purplish brown variety. Sections parallel to (OIO) give extinction angles between 42° and 48° . The specific gravity is 2.83. Chemical analysis is as follows :—

For Comparison analyses B, C and D are inserted.

			A	B	C	D
SiO ₂	53.57	53.12	52.98	52.00
TiO ₂	1.23	1.40	0.62	...
Al ₂ O ₃	17.16	15.72	14.53	18.76
Fe ₂ O ₃	3.50	3.72	3.38	9.38
FeO	10.22	9.10	10.05	1.14
MgO	2.04	2.74	3.66	2.04
CaO	8.93	9.94	7.49	9.23
Na ₂ O	3.65	3.54	3.43	4.17
K ₂ O	1.15	0.75	1.34	1.66
H ₂ O (+)	0.40 (Ignit)	0.15	1.88	2.68
H ₂ O (-)		0.21	0.48	
P ₂ O ₅	0.36	0.64	0.32
MnO ₂	0.04	—
Total				
Sp. gr.				

- A. Rock under description. Analysed by G. P. Contractor.
 B. Andesite. Malbar Hill. (anal. Mr. Naidu and Prof. Mathur.) Ref. No. 15.
 C. Andesite. Between Race Hill & Sewri (Washington).
 D. Andesite. (Anal. E. Frankland) Busielaw, Pentlands, Edinburgh, Mem. Geol. Surv. Grt. Britain. 'Analyses of Rocks and Minerals'. No. 182 p. 48. Ref. No. 41.

BASALT

Locality :—One of the quarries between Kurla and Ghatkoper railway stations, about 25 yards north-west of 'Kurla H Cabin'. Megascopically the rock is dark in colour with a crystalline aspect, imparting an intermediate textural characteristic of anamesites. Under the microscope (Fig. 13) the texture falls between intersertal and subophitic. Larger crystals of felspar give symmetrical extinction as high as 35° , pointing to its identity as labradorite of $Ab_{40} An_{60}$ composition. A few laths average more basic in composition and give extinction angles upto 40° . The smaller laths of the groundmass (0.15 to 0.45 mm.) give extinctions up to 30° on the Albite twin, characterising the labradorite of $Ab_{45} An_{55}$. Some of the larger crystals of labradorite (1.8×1.2 mm.) display beautiful "graphic texture." Pyroxene is pale mauve coloured, often tinted greenish and is non-pleochroic. However, all the crystals are not of uniform composition. Some of the crystals, pale green in transmitted light and giving low extinction angles, probably suggest the non-aluminous variety. Extinction angles measured on sections approximately parallel to (OIO) averaged to 30° , highest recorded being 45° . However, the major portion of pale mauve variety may be taken as augite. Iron ores occur as pieces and bars. The platy grains may be of ilmenite in view of the presence of titanitic acid—2.12% and the characteristic shape of the mineral. Specific gravity is 2.91.

CHEMICAL COMPOSITION

Analysis of the fresh specimen gave the following result—A. Analyses B, C, D and E are added for comparison.

	A	B	C	D	E	Mol. Proportion.
Si O ₂ ...	49.60	48.64	49.34	50.61	48.78	0.826
Ti O ₂ ...	2.12	1.42	2.19	1.91	1.39	0.026
Al ₂ O ₃ ...	16.10	14.22	13.30	13.58	15.85	0.158
Fe ₂ O ₃ ...	4.73	2.64	5.01	3.19	5.39	0.029
FeO ...	9.17	10.52	7.85	9.92	6.34	0.127
MgO ...	5.15	5.36	5.63	5.46	6.03	0.128
CaO ...	10.85	11.51	9.37	9.54	8.91	0.193
Na ₂ O ...	2.28	2.67	4.04	2.60	3.18	0.036
K ₂ O ...	0.87	1.04	0.88	0.72	1.68	0.009
H ₂ O ...	1.00	2.70	1.44	1.70	1.76	
	(Igni)					
P ₂ O ₅ ...	—	—	0.99	—	0.47	
MnO ..	—	—	0.20	0.16	0.29	
Total ...	101.87	100.72	100.24	99.39	100.07	
Sp. Gr. ...	2.91	2.99	2.90			

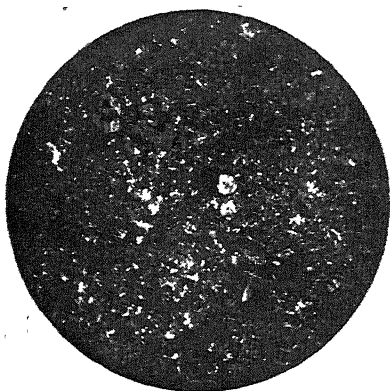


Fig. 1.

Augite Granophyre, Marol quarry.
A = Augite. Groundmass consists of
Quartz and Felspar in intimate inter-
growth, with crystals of Augite.

× 29

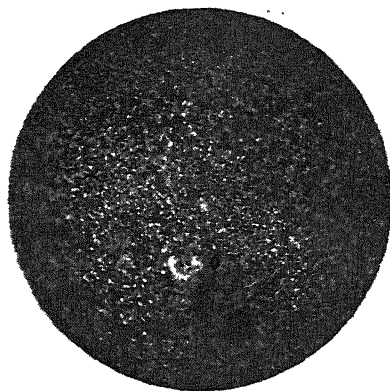


Fig. 2.

Altered Granophyre, Jogeshwari.
Groundmass consists of cryptocrystal-
line matrix. Orthoclase = O.

× 29 Nicols Crossed.

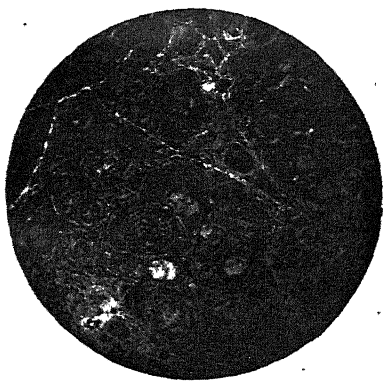


Fig. 3.

Perlite, Santacruz-Khar area

× 29

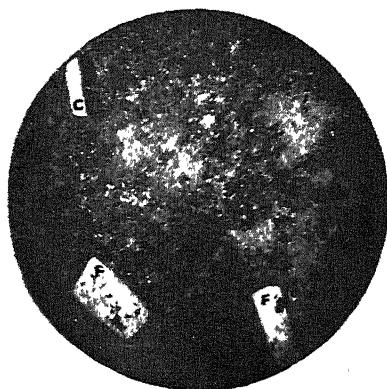


Fig. 4.

Felsite, Santacruz Khar area, with
felsitic groundmass and phenocrysts of
felspar=F. Carlsbad twin=C.

× 29 Nicols Crossed.

Norm Minerals calculated from (A).

	(C)	(B)	(A)	
Quartz	3.00	Salic =57.16
Orthoclase	5.00	6.17	5.00	
Albite	34.06	22.58	18.86	
Anorthite	15.57	23.69	30.30	
Diopside	20.34	27.73	18.18	Femic =42.24
Hypersthene	7.74	2.69	13.38	
Olivine	2.44	8.62	...	
Magnetite	7.19	3.82	6.73	
Ilmenite	4.10	2.69	3.95	
Apatite	2.35	
Total ...	99.53	97.99	99.40	
Water ...	1.44	2.70	1.00	
Total ...	100.23	100.69	100.40	

C. I. P. W. Classification of (A)

Class ...	Salfemane
Order 5 ...	Gallare
Rang 4 ...	Auvergnase
Subrang 3 ...	Auvergnose

- A. Basalt from Kurla, Salsette, Bombay. (anal. by G. P. Contractor)
- B. Basalt from Mt. Girnar, Kathiawar. (anal. M. S. Krishnan) p. 418. Col. 4 Ref. No. 18. R. Geol. S. I. Vol. LVIII.
- C. Basalt from Pawagad, B'by Presidency. (anal. R. K. Saksena) Dr. V. S. Dubey. Ref. No. 36. Ph. D., Thesis Pt. I. Lond. University (1929).
- D. Deccan Trap Average of 11 Analyses (including one from Rajmahal). (Washington) Ref. No. 10 p. 136. R. G. S. I. LVIII.
- E. Average composition of Basalts (161 analyses) From R. A. Daly Ref. No. 27. p. 27 Col. 54. "Igneous Rocks and their Origin."

OLIVINE BASALT AND PORPHYRITIC OLIVINE BASALT.

Locality :—Higher middle part of the Hill-(538') 19°-8'-15" : 72°-55'. In hand specimen the rock appears fine grained, sub-aphanitic and blackish in colour. In thin sections (Fig. 8) the rock consists of numerous microphenocrysts of nearly fresh to completely altered (serpentinised) olivine (0.12 to 0.6 mm.) and a number of pale purple subhedral and platy crystals of augite measuring 1.2 mm. in length, in a groundmass of minute laths of plagioclase. The texture of the rock approaches basaltic type, while at places microlites are fluxionally arranged. The laths in the groundmass are apparently

labradorite of the composition $Ab_{48} An_{52}$ while a few minute phenocrysts are basic labradorite of the value $Ab_{30} An_{70}$. Augite is an aluminous monoclinic variety, giving extinction angles as high as 45° . Olivine crystals have a tendency towards idiomorphism and are often fresh and hence colourless. The mineral has altered to serpentine and in some cases to iddingsite. It has also altered typically to calcite and magnesite. Iron ores are present. Interstitial colourless glass is present.

OLIVINE BASALT-PORPHYRY

Locality :—From the top of the Hill (400'), a mile and a half north-west of Pachkoli village ($19^\circ-8' : 72^\circ-54'$). It is near Vehar lake. This type is a fine grained crystalline rock, enclosing minute laths of felspar visible to the naked eye. Under the microscope (Fig. 9) the texture is seriate-porphyritic, with interstitial augite and olivine. The felspar of the groundmass is little more acid, perhaps $Ab_{43} An_{57}$ (extinction angle being 30°) than that of the phenocrysts which are near to $Ab_{30} An_{70}$. Red brown haematitic and in part iddingsitic pseudomorphs after olivine are also seen. Augite is common purplish variety with extinction angle ranging upto 40° . The alteration of olivine into haematite and the formation of net work of iron oxide suggests that the olivine belongs to the iron rich variety fayalite. The opaque iron ores occur as bars and needles. Apatite is practically absent.

AMYGDALOIDAL BASALT (TUFF LIKE)

Locality :—This type of rock occupies the upper vesicular or amygdaloidal basic portion of the Hills (538') and (400'). It is also found in the higher grounds east of Vehar Lake. Megascopically the rock shows purplish grey colour with a number of cavities and amygdales set in an earthy and dull matrix. Some of the vesicles are spherical while others are elongated in the direction of the flow. In thin sections (Fig. 14) these rocks show fine and uniform texture and consist essentially of the intergrowth of felspar laths. Between the laths are wedged very small granules of augite and magnetite. Olivine is present in a subordinate amount, pseudomorphs after serpentinous, brown limonitic, and deep red iddingsitic minerals. The texture approaches porphyritic type and is characterised by the glomero-porphyritic groups of augite and micro-porphyritic felspars. Felspars are nowhere to be found in perfectly fresh condition, the laths enclosing patches and shreds of chloritic or chlorophaeitic or limonitic matter. Bigger well developed crystals of augite give extinction angle averaging to 37° . These rock types are basic

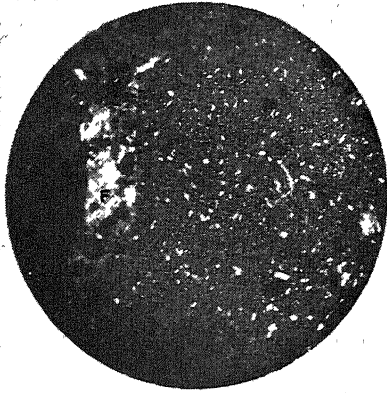


Fig. 5.

Rhyolite Tuff, Santacruz Khar area.
F=Corroded felspar.



Fig. 6.

Granophyric Trachyte, Kurla.
× 50 Nicols Crossed.

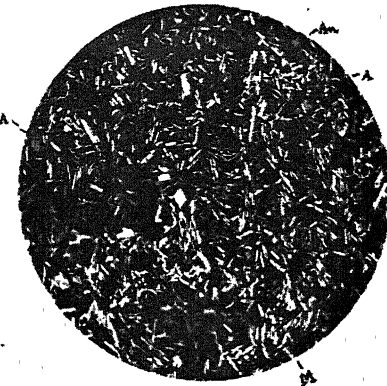


Fig. 7.

Andesine Andesite, Danda. Felted texture with granules of Augite=A. Laths of Andesine = An and Magnetite = M.

× 29.

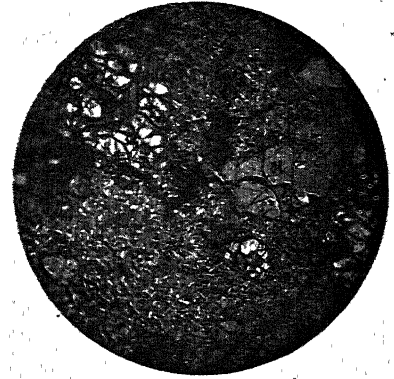


Fig. 8.

Porphyritic Olivine Basalt, Vehar Lake.

× 29 Nicols Crossed.

in composition giving silica percentage as low as 41.20 and characterised by a fairly large proportion of interstitial glass. The chief minerals present in the vesicular cavities and amygdals are chlorite and minerals allied to that family, zeolites, calcite and silica. Chabazite is also of common occurrence. Where brown palagonitic material is in fairly large quantity, zeolites are rare but it is generally associated with delessitic matter. Another interesting fact is that where chlorophaeite is in higher proportion, chabazite is present. This is in accord with Dr. Fermor's observations with regard to chabazite in the "Lavas of Bhusawal". Of the green minerals delessite occurs in great abundance especially in the central part of small globular vesicles, celadonite being quite subordinate in amount. Small globules free from zeolitic minerals were taken out, crushed and analysed.

CHEMICAL COMPOSITION

In the following table an analysis of the mineral is given in column (A). For comparison are added the analyses B, C, D and E of delessite, debantite celadonite and glauconite respectively.

		A	B	C	D	E
SiO ₂	31.91	32.00	31.32	54.24	49.50
Al ₂ O ₃	15.22	17.33	10.89	3.52	8.37
Fe ₂ O ₃	15.63	1.19	2.86	12.64	16.07
FeO		12.45	24.82	4.90	6.47
MnO	n. d.	...	0.39	0.23	...
MgO	23.10	20.42	19.33	6.65	2.60
CaO	0.73	1.57	0.92	0.91	1.07
K ₂ O	n. d.	6.77	6.59
Na ₂ O	n. d.	...	0.29	0.36	0.58
H ₂ O	5.01 (at 105°)	15.45	11.48	9.61	8.54
Total	91.60	100.41	102.30	100.43	99.79

- A. Delessite from Salsette Island, Bombay. (Anal. by G. P. Contractor).
- B. Delessite. Bowling. From Dana's "A System of Mineralogy" 1906 p. 660.
- C. Debantite Average of 7 analyses. Calculated from Dana' s.p. 659.
- D. Celadonite. Average of 4 analyses. Calculated from Dana' s.p. 683.
- E. Glauconite. Average of 11 analyses. Calculated from Dana' s. p. 684.

From the chemical analyses it is seen that the mineral (A) is similar in composition to delessite (B). There is a wide range of magnesia content of these minerals and this variation is a good 'chemical test' for distinguishing these allied minerals. Debantite (C) is very close to delessite but its higher iron oxide content differentiates it from the latter mineral. Optically (Works referred—Ref. Nos. 10,38 and 44) the mineral appears pale green or lemon yellow to colourless and is distinctly pleochroic. The mineral is fibrous and when examined with a quartz plate shows the slow vibration direction parallel to the laminae.

DOLERITE AND OLIVINE DOLERITE

Locality :—Dolerite,—from two miles west of Thana railway station. Olivine Dolerite,—from the top of the Hill (237'), west of Jogeshwari ($19^{\circ}-8' : 72^{\circ}-51'$). The rock is holocrystalline hypidiomorphic even grained type with vitreous lustre. It is dirty grey in colour. Shining laths of felspar and dull black grains of augite are visible to the naked eye. Microscopically (Fig. 10) the rock appears crowded with crystals of augite, laths of felspar and black magnetite. Augite is often surrounded by the laths of felspar presenting an ophitic texture. Felspar 0.45 to 2.10 mm. long with Albite lamellation (Carlsbad twins are also often seen) have extinction angles upto 42° to 50° , indicating medium to basic labradorite. Augite crystals approaching idiomorphism are pale mauve in tint. The high percentage of titanitic acid (2.16%) and the characteristic colour probably suggests the variety to be titan-augite. Iron ores are present in abundance and include both ilmenite and magnetite. The olivine occurs in the form of small grains and euhedral crystals. The common alteration product is a net work of deep brown iron oxide suggesting that it belongs to iron rich variety fayalite. A rough estimation of the minerals of the rock type—dolerite—gave the following figures :—Plagioclase=32.00, Pyroxene=23.00, Iron ores=18.00, Altered Products = 27.00. Total = 100.00.

CHEMICAL COMPOSITION

The results of the analysis of the rock under consideration are tabulated in column (A). For comparison analyses B, C, and D are added.

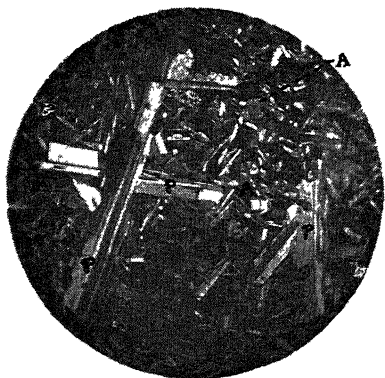


Fig. 9.
Olivine Basalt-porphyry, Vehar Lake.
× 29 Nicols Crossed.

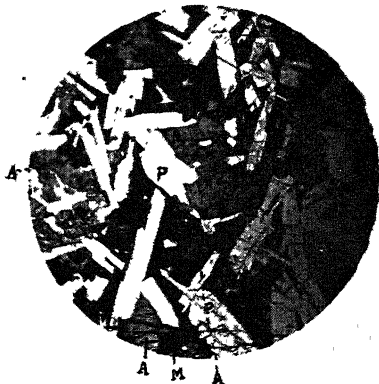


Fig. 10.
Dolerite, Vehar Lake, also Jogeshwari.
× 29.

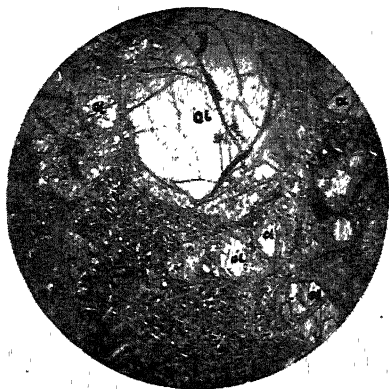


Fig. 11.
Oceanite, Hill 538'. Ol=Olivine
showing alteration to Serpentine Anthophyllite and Iron Ores along cracks and Margins.
× 29 Nicols Crossed.

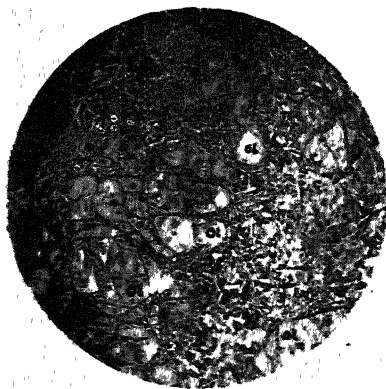


Fig. 12.
Ankaramite, Hills 538' and 400'.
× 29.

	A	B	C	D
SiO ₂	47.30	47.72	47.02	47.64
TiO ₂	2.16	2.56	2.56	1.27
Al ₂ O ₃	14.33	14.54	12.46	14.15
Fe ₂ O ₃	14.31	1.83	5.80	5.18
FeO		8.79	9.25	7.96
MgO	5.93	5.57	4.51	7.38
CaO	11.00	14.09	9.90	11.71
Na ₂ O	3.10	2.99	4.92	2.38
K ₂ O	0.97	1.62	1.50	0.71
H ₂ O	1.09	0.99	1.54	1.63
P ₂ O ₅	n.d.	—	0.69	0.09
MnO	n.d.	—	0.19	0.33
S, Cr ₂ O ₃ , V ₂ O ₃ ...	n.d.	—	—	0.10
Total	100.19	100.75	100.34	100.53
Sp. Gravity	3.00	3.03	2.90	3.01

- A. Dolerite from Salsette Island, Bombay. (Anal. by G. P. Contractor).
- B. Olivine-Gabbro from Girnar and Osham Hills, Kathiawar. (Anal. M. S. Krishnan) Ref. No. 18. pp. 380-424.
- C. Basalt from Pawagad. (anal. Dr. Dubey) Ref. No. 36.
- D. Dolerite. (Anal. W. Pollard) From "The Tertiary Igneous Rocks of Skye" A. Harker. Ref. No. 23.

From the table it is clear that the Salsette Island Dolerite has a very close chemical similarity to the types occurring in the Deccan Trap flows of Kathiawar (B) and Pawagad (C). Sp. gravities are also almost the same.

OCEANITE AND ANKARAMITE.

Locality :—The rocks are mainly confined to the Hills 538' and 400' situated east of Vehar Lake and a mile and a half N. E. of Pachkoli village (19°-8' : 72°-54'). The hills afford interesting

studies in the phenomenon of gravitative-differentiation and is treated in the following pages. The rocks present some megascopic difference, in the presence of greater amount of olivine phenocrysts in the oceanites than in the Ankaramites in which there is an excess of normative augite over normative olivine. Oceanites appear greenish dark in colour with abundant small crystals of fresh greenish yellow olivine. Ankaramites present brown pinkish coloration with cherry red bands of iron oxide. Both the types are holocrystalline and granular in aspect. Microsections (Figs. 11 and 12) show an aphanitic groundmass composed of thin laths of plagioclase, grains of purplish pyroxene and granular iron ores. Olivine is practically absent in the groundmass but its presence in the form of phenocrysts imparts a porphyritic texture to the rocks. Plagioclase is less basic variety e.g. $Ab_{65} An_{35}$. The extinction angle on the Albite lamellae gives an average reading of 35° and determines the species to be of $Ab_{40} An_{60}$ composition. More basic variety—basic labradorite—is also seen. Some laths show graded extinction. Plagioclase in its behaviour towards augite grains and granules imparts an ophitic to sub-ophitic texture to the groundmass. The mauve coloured augite is plentiful; the extinction angles measured on cleavage are 57° to 59° . A few crystals with low extinction angles (19° to 23°) and feebly birefringent may be referred to monoclinic magnesium pyroxene variety—Clinoenstatite. However, the majority of the pyroxene may be taken to be titaniferous augite ($TiO_2 = 2.12\%$), although the extinction angle is higher than any recorded for such varieties. Occasional bands of inclusions and structure similar to schillerisation are not infrequently seen. Olivine phenocrysts are present in both fresh and altered conditions and vary from 0.7 to 4.5 mm. in length. The common alteration product is green feebly fibrous and felted serpentine. Other alteration products are anthophyllite, magnesite or calcite. Red ferruginous stains are frequently seen. In the groundmass are seen occasionally a number of vermicular patches of light green fibrous mineral much allied to serpentine. Magnetite, titaniferous variety, is also present.

CHEMICAL COMPOSITION

The result of analysis of this (Oceanite) rock is set forth in the following table. Similar ultra-basic rocks from various localities are also tabulated for comparison.

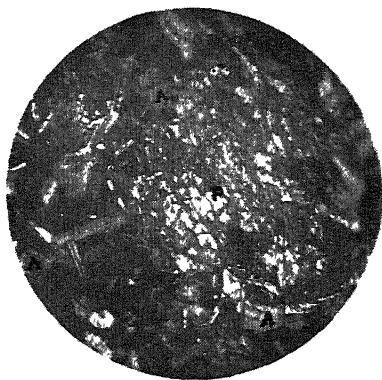


Fig. 13.

Basalt, Kurla, showing groundmass consisting of Plagioclase=P (See Graphic texture), Augite=A and Magnetite = M.

× 50 Nicols Crossed.

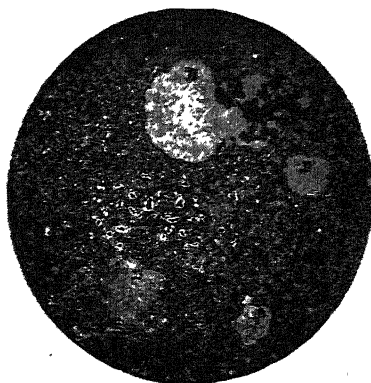


Fig. 14.

Amygdaloidal Basalt, Vehar Lake, showing spherules of Delessite = D, glomeroporphyritic group of Augite = A, and dark chlorophytic matter.

× 16.



Fig. 15.

A tram line cutting in the Hills (538') and (400'), situated about a mile and half N. E. E. of Pachkoli Village ($19^{\circ}-8'$: $72^{\circ}-54'$).

The rock shows spheroidal weathering and from here the ultrabasic rocks were collected.

	A	B	C	D	E	Mol. Proportion.
SiO ₂ ...	43.26	43.45	43.96	41.61	45.60	0.721
TiO ₂ ...	2.12	—	2.07	2.25	—	0.026
Al ₂ O ₃ ...	10.85	—	9.84	10.86	8.30	0.106
Fe ₂ O ₃ ...	3.01	—	3.04	2.31	2.30	0.019
FeO ...	7.80	—	10.40	7.46	10.20	0.108
MgO ...	18.32	18.18	20.70	21.06	21.70	0.458
CaO ...	10.31	—	7.93	9.01	7.50	0.184
Na ₂ O ...	1.23	—	1.48	1.15	1.30	0.019
K ₂ O ...	0.53	—	0.62	0.19	0.40	0.005
H ₂ O ...	3.60 (Igni)	—	0.01	1.22	0.60	
MnO ...	—	—	—	0.16	0.10	
P ₂ O ₅ ...	—	—	2.25	0.10	0.30	
Total ...	101.03		100.30	100.38	100.00	

Norm Minerals calculated from A.

Orthoclase	2.78	} = Salic 35.54
Albite	9.96	
Anorthite	22.80	
Diopside	22.38	} = Femic 61.47
Olivine	30.73	
Magnetite	4.41	
Ilmenite	3.95	

Total	97.01
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Water (Igni)	...	3.60
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Total	100.61
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G. I. P. W. Classification of (A).

Class IV	Dofemane.
Order 2	Scotare.
Section 3	Texiare.
Rang 1	Texase
Section 2	(Domic).
Sub-Rang	Uvaldose.

A. Oceanite from Salsette Island, Bombay. (Anal. by G. P. Contractor).

- B. "Oceanites and Ankaramites" from Kathiawar, Bombay. L. L. Fermor. Ref. No. 13. p. 19. R. Geol. Sur. India Vol. LXVI pt. I. (1932).
- C. "Felspathic picrite." From J. P. Iddings Ref. No. 28. p. 589 Table 122, Col. 11. (Lacroix refers it as "picrite-felspathique"—Oceanite—Compt. rend., 155 p. 539 (1912). "Igneous Rocks" (1913) Vol. II.
- D. "Picrite Dolerite". From Bowen. Ref. No. 29. p. 154, Table XII.
- E. Oceanite (ultrabasic olivine rich basalt) Mean of 10 analyses. Tyrell, Principles of Petrology, 1926, p. 131.

Partial chemical analysis of oceanite from Kathiawar (Col. B) as given by Dr. Fermor bears a very close resemblance to Salsette type. Salsette rock is also almost identical with oceanites from Reunion (Col. C) and a picrite-dolerite from Isle of Syke (Col. D).

CHEMICAL COMPOSITION
(Ankaramite)

	A	B	C	D	E	Mol. Proportion.
SiO ₂ ...	44.90	46.73	46.80	47.72	44.75	0.748
TiO ₂ ...	2.88	1.90	1.80	2.56	3.45	0.035
Al ₂ O ₃ ...	11.00	9.30	7.86	14.54	13.22	0.108
Fe ₂ O ₃ ...	1.65	3.25	4.26	1.83	1.20	0.010
FeO ...	9.57	5.37	7.89	8.79	10.50	0.132
MgO ...	15.98	14.93	14.79	5.57	10.85	0.399
CaO ...	10.97	14.50	10.96	14.09	11.50	0.195
Na ₂ O ...	1.47	1.32	2.93	2.99	1.95	0.023
K ₂ O ...	0.75	1.14	0.83	1.62	1.27	0.007
H ₂ O (—) ...	} <i>n. d.</i>	0.50	1.10	0.99	1.62	
H ₂ O (+) ...		0.45	0.80			
P ₂ O ₅ ...	—	0.25	0.19	—	0.38	
MnO ...	—	0.29	0.30	—	—	
Cr ₂ O ₃ ...	—	0.19	—	—	—	
Total ...	99.17	100.12	100.51	100.75	100.69	
Sp. Gravity ...	2.98		2.97 (mean)	3.03		

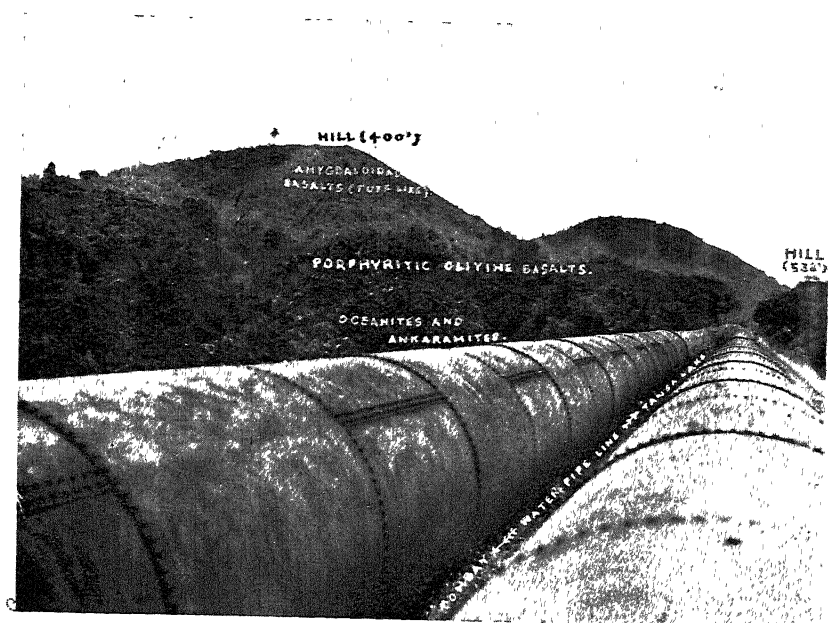


Fig. 16.
View of the Hill (400') near Vehar Lake. It is mainly composed of ultrabasic and basic rocks at different levels.

Norm Minerals calculated from (A).

Orthoclase	3.89	} = Salic
Albite	12.05	
Anorthite	18.90	
Diopside	28.17	} = Femic
Olivine	27.45	
Magnetite	2.32	
Ilmenite	5.32	
Total					98.10	

- A. Ankaramite from Salsette Island, Bombay (anal. G. P. Contractor).
- B. Ankaramite (Ultrabasic olivine basalt) anal. W. H. & F. Herdman. "The Petrology of Jan Mayen" Trans. Roy Soc. Edin. (1926) Vol. LIV, p. 757.
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POSSIBLE DIFFERENTIATION IN THE MAGMA.

The field occurrence of the different types of lavas in this area ranging from ultrabasic to acid can hardly be assigned to separate magmatic origin in view of the recent studies in the science of petrogenesis. The hypothesis of crystallization-differentiation, and the phenomenon of gravitative-sinking of the early formed crystals, on which a large amount of literature by Bowen, Daly, Vogt, Harker, A. Holmes, Washington, and others is now available, is made use in explaining the above mentioned rock types found in this area. Dr. A. Holmes' hypothesis of the existence of peridotitic melt below the basaltic layers may hold good in other parts of the world, but in the present case the mode of occurrence of the ultrabasic and acid rocks points to their olivine rich basalt parentage rather than their derivation from the original ultrabasic melt. Dr. Fermor discussing the origin of acid and basic types in the Deccan Trap flows occurring in Kathiawar and Gujrat assume the existence of a magma which subsequently differentiated into two portions, an acid and a basic and that "according as the acid or the basic portion of the magma was tapped, so were the erupted lavas, rhyolites or basalts." Same holds true in the present area. Intermediate type, Andesine Andesite, which is prevalent on the west coast of the Island may be taken to be an early differentiate from the basaltic magma. This Andesite-Basalt association may well be explained if we imagine the original magma basic. The early formed crystals of olivine, labradorite and augite will sink leaving a

residuum less basic and andesitic in character. On further phenocrystal sinking of olivine, labradorite and augite the residuum magma becomes acidic and takes up a composition nearing rhyolites or felsites. The trachytic suit of rocks may best be referred to the differentiation of basaltic magma as well. Here it is interesting to note that Prof. K. K. Mathur treating the genesis of acid rocks found in association with the Deccan Trap Lavas, observes that the hypothesis of pure melting of sial 'palingenesis', and magmatic assimilation, i. e. the solution of the sediments by the magma may find an application for the origin of these acid rocks. However, this hypothesis may find an application in other parts of India, the absence of certain data in the present area makes it inapplicable to the acid rocks of Salsette Island. Also Daly's hypothesis of the genetic connection between the limestones and the trachytic types cannot be applied here due to the complete absence of carbonate rocks in the whole island. Another interesting observation is the occurrence of free silica, though in quite a subordinate amount in granophyres and trachytes. This points to the sinking or separation of excess olivine from the parent olivine rich basaltic magma at early stages. Due to this early segregation of the excess olivine crystals they are left unresorbed, leaving residual magma with free silica. Regarding the ultrabasic rocks, they may be taken to represent the other pole of differentiation from the original olivine rich basaltic melt. The rock types from the lower parts of the Hills 538' and 400' (Figs. 15, and 16) contain large percentage of olivine phenocrysts, giving them high specific gravities. As we ascend the Hills the percentage of mafic minerals falls and at higher levels we come across olivine basalts overlain by basic tuffs charged with a few crystals of olivine. These observations are in direct accordance with the phenomenon of crystal-sinking. Similar observations in the Deccan Trap flows of India have been made by Dr. Fermor and Dr. Dubey. Another interesting fact is the occurrence of phenocrystal olivines, rich in forsterite molecule ($2\text{MgO} \cdot \text{SiO}_2$) in the lower flows, while in the upper flows we find more of augite and less of olivine, rich in fayalite molecule ($2\text{FeO} \cdot \text{SiO}_2$). This difference in the nature of olivine is characteristically shown by the resulting alteration products. While the olivine crystals from the lower flows have altered to Calcite or Magnesite (MgCO_3) and serpentine ($3\text{MgO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$), the alteration products of olivines from the upper flows are Iddingsite (hydrated iron and magnesium silicate), Haematite, and other iron oxides. This is in accord with the order of crystallization given by Bowen and also supports the view that the ratio of MgO to FeO in olivine decreases with the fall of temperature and hence the crystallization of olivines rich in Fayalite molecule ($2\text{FeO} \cdot \text{SiO}_2$) at a lower

temperature in the upper flows, and Forsterite molecule ($2\text{MgO} \cdot \text{SiO}_2$) at a higher temperature and in the lower flows. Dr. Dubey makes similar observations in Pawaghad Hill, near Baroda. Very recently Dr. Fermor has reported the occurrence of Oceanites, Ankaramites, and Limburgites from Kathiawar. The optical investigations by W. D. West of olivines, feldspars and other phenocrysts has led Dr. Fermor to conclude that "these ultrabasic rocks must have crystallized from melts of their own composition." However, this may be true for the Kathiawar rocks, the present ultrabasic suit of Salsette Island both from the microscopical studies and field observations show that they are formed by the gravitative-sinking of the early formed crystals. While the 'ultrabasic' rocks of Bhusawal, Pawagad and Salsette find their common origin in the gravitative differentiation, the Kathiawar types have originated independently from the original ultrabasic melt. With regard to this Prof. Mathur remarks :—"It appears that olivine-bearing associates of the Deccan Trap may thus have two types of origin, depending on whether they crystallized from the 'normal' basalt or from an ultrabasic melt."

CONCLUSIONS

The rocks of the Salsette Island are sub-aerial basaltic lava flows of great lateral extent in which the subsequent intrusive phases are represented by the rock types such as Oceanites, Ankaramites, Dolerites, Trachytes, Granophyres, Felsites, Rholites etc. The pyroclastic rocks in the form of breccias, Rhyolite Ash, Glassy Tuffs etc., occur at different horizons. They may be taken to locate the existence of orifices in the midst of fissures, from which pyroclastic material was ejected at one time or other. Probably the grounds of Santacruz-Khar, Jogeshwari and Marol Caves represent the old volcanic orifices.

Four new areas containing the acid differentiate are recorded in this paper. They are :—(1) Felsites, Rhyolites and Perlites of the Santacruz-Khar area, (2) Granophyric Trachytes of Kurla, (3) Altered Granophyres and Rhyolite Ash of Jogeshwari Caves area, and (4) Augite Granophyres of Marol hills.

As regards the occurrence of Ultrabasic rocks in this Island, it has been pointed out that they were never being recorded previous to this paper. They include Oceanites, Ankaramites and Olivine rich Dolerites.

Chemically the present suit of rocks embraces types ranging in silica percentage as high as 71 to as low as 43. In the more acid varieties of the series the percentage of total alkalis rise as high as 10.76, and is characterised by an excess of soda over potash. The trachytes, granophyres, and felsites thus present affinities to the alkaline rocks. The dolerites and the anamesites belong to the calc-alka-

li class and may be compared with the plateau basalts.

In the ultrabasic members of the series the percentages of magnesia and lime are as high as 18.32 and 10.00, respectively. These higher values are compensated by very low alkali contents thus indicating that these ultrabasic members belong to lime-rich series (Pacific Type). This inference is further supported by the Variation diagram.

Basalts present the ordinary plateau type variety while the intermediate andesites are rich in microlites of andesine-plagioclase.

The rocks of this island when compared with the types from Kathiawar and Pawagad show that similarity exists both at the basic and acid ends. Because of the similarity, both chemical and mineralogical, between the felsites of this island and those of Pawagad, it may be deduced that this acid intrusive phase which is decidedly younger than the Deccan Trap, corresponds to the Miocene period (Dr. V. S. Dubey calculates from the helium ratio an age of 5.5-9 million years for an acid felsite from Pawagad Hill. Abst. of Papers, Geology Section, Indian Science Congress, Bombay, 1934.).

The sequence in order of crystallization is probably as follows :—Oceanites and Ankaramites, Olivine Dolerites, Olivine Basalts, Basalts, Olivine free Dolerites, Andesine-Andesites, Augite Granophyres, Trachytes, Felsites and Rhyolites.

Briefly it may be stated that the petrological sequence of Girnar in Kathiawar and Pawagad in Gujrat continues all the way down along the coast through Rajpipla State, Bassein, Salsette, Bombay to an unknown distance in the South.

APPENDIX A.

CHEMICAL ANALYSIS

In the following table is given all the analyses given before separately with a view to study the variation in the chemical composition of the magma.

	1	2	3	4	5	6	7	8	9
SiO ₂	71.00	67.00	66.20	62.91	53.57	49.60	47.30	44.90	43.26
TiO ₂	0.59	0.60	0.75	0.23	1.23	2.12	2.16	2.88	2.12
Al ₂ O ₃	16.35	14.55	13.12	14.97	17.16	16.10	14.33	11.00	10.85
Fe ₂ O ₃	2.73	1.06	3.00	0.72	3.50	4.73	14.31	1.65	3.01
FeO	1.03	3.05	1.10	3.80	10.22	9.17		0.57	7.80
MgO	0.52	1.37	1.19	0.43	2.04	5.15	5.93	15.98	18.32
CaO	1.41	5.40	1.90	4.40	8.93	10.85	11.00	10.97	10.31
Na ₂ O	4.32	3.78	6.01	5.85	3.65	2.28	3.10	1.47	1.23
K ₂ O	3.05	2.60	4.65	4.91	1.15	0.87	0.97	0.75	0.53
H ₂ O	—	1.20	3.20	2.00	0.40	1.00	1.09	—	3.60
Total	99.52	100.61	101.12	100.22	101.85	101.87	100.19	99.17	101.03

NORM

	1	2	3	4	5	6	7	8	9
Quartz ...	30.84	22.56	13.74	1.80	3.54	3.00
Orthoclase ...	17.79	15.57	27.24	28.91	6.67	5.00	...	3.89	2.78
Albite... ...	36.15	31.44	41.39	49.25	30.39	18.86	...	12.05	9.96
Anorthoclase..	6.95	15.01	27.24	30.30	...	18.90	22.80
Diopside	9.68	7.50 8.32 (Acmit- te)	15.08	14.19	18.18	...	28.17	22.38
Wollastonite	1.86
Corundum ...	3.47
Hypersthene ...	1.30	2.29	11.55	13.33
Olivine	27.45	30.73
Haematite ...	1.60
Magnetite ...	1.62	1.39	0.23	0.93	5.10	6.73	...	2.32	4.41
Ilmenite ...	1.06	1.22	1.37	0.46	2.28	3.95	...	5.32	3.95
Total ...	100.78	99.16	98.79	98.29	100.96	99.40	...	98.10	97.01
Water ...	n. d.	1.20	3.20	2.00	0.40	1.00	3.60
Total ...	100.78	100.36	101.99	100.29	101.36	100.40	...	98.10	100.61

1. Felsite	Sp. Gravity	...	2.42
2. Augite Granophyre	"	...	2.52
3. Rhyolite Tuff	"	...	2.26
4. Granophyric Trachyte	"	...	2.56
5. Andesine Andesite	"	...	2.83
6. Basalt	"	...	2.91
7. Dolerite	"	...	3.00
8. Ankaramite	"	...	2.98
9. Oceanite	"	...	3.02

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(Received, June 29, 1936.)

THE SOLUTION OF THE PROBLEM OF SAINT VENANT

By

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Let an isotropic elastic body be subject to no external forces. Then the equations of equilibrium of the body reduce to

$$\frac{\partial N_1}{\partial x} + \frac{\partial T_3}{\partial y} + \frac{\partial T_2}{\partial z} = 0$$

$$\frac{\partial T_3}{\partial x} + \frac{\partial N_2}{\partial y} + \frac{\partial T_1}{\partial z} = 0$$

$$\frac{\partial T_2}{\partial x} + \frac{\partial T_1}{\partial y} + \frac{\partial N_3}{\partial z} = 0$$

where (N_1, N_2, N_3) ; (T_1, T_2, T_3) are respectively the normal and tangential stresses connected with u, v, w the components of the molecular displacement by the following relations :

$$N_1 = \lambda \Delta + 2\mu \frac{\partial u}{\partial x} \quad , \quad T_1 = \mu \left(\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} \right)$$

$$N_2 = \lambda \Delta + 2\mu \frac{\partial v}{\partial y} \quad , \quad T_2 = \mu \left(\frac{\partial w}{\partial x} + \frac{\partial u}{\partial z} \right)$$

$$N_3 = \lambda \Delta + 2\mu \frac{\partial w}{\partial z} \quad , \quad T_3 = \mu \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right)$$

where λ and μ depend upon the material of the body [μ being the modulus of rigidity and $(\lambda + \frac{2}{3}\mu)$ the modulus of elasticity or the modulus of compression] and Δ is the cubical dilatation.

If further we are given that

$$N_1 = N_2 = T_3 = 0$$

we get

$$N_1 = \lambda \Delta + 2\mu \frac{\partial u}{\partial x} = 0$$

$$N_2 = \lambda \Delta + 2\mu \frac{\partial v}{\partial y} = 0$$

$$T_3 = \mu \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) = 0$$

The first two equations furnish us with

$$\frac{\partial u}{\partial x} = \frac{\partial v}{\partial y} \quad \text{and} \quad \frac{\partial u}{\partial y} = -\frac{\partial v}{\partial x} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\therefore \Delta = 2 \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 2 \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}$$

$$\text{Hence } N_1 = \lambda \left(2 \frac{\partial u}{\partial x} + \frac{\partial \omega}{\partial z} \right) + 2\mu \frac{\partial u}{\partial x} = 0$$

$$\therefore \frac{\partial u}{\partial x} + \sigma \frac{\partial \omega}{\partial z} = 0 \text{ and } \frac{\partial v}{\partial y} + \sigma \frac{\partial \omega}{\partial x} = 0 \text{ where } \sigma = \frac{\lambda}{2(\lambda + \mu)}$$

$$\therefore \frac{\partial u}{\partial x} = \frac{\partial v}{\partial y} = -\sigma \frac{\partial \omega}{\partial x} \quad (2)$$

$$\therefore \Delta = (1 - 2\sigma) \frac{\partial \omega}{\partial z} = -\frac{2\mu}{\lambda} \frac{\partial u}{\partial x} = -\frac{2\mu}{\lambda} \frac{\partial v}{\partial y} = \frac{\mu}{\lambda + \mu} \frac{\partial \omega}{\partial z}.$$

σ is known as 'Poisson's ratio.'

Next consider the equations of equilibrium when there are no external forces acting upon the body. They are

$$\frac{\partial N_1}{\partial x} + \frac{\partial T_3}{\partial y} + \frac{\partial T_2}{\partial z} = 0$$

$$\frac{\partial T_3}{\partial x} + \frac{\partial N_2}{\partial y} + \frac{\partial T_1}{\partial z} = 0$$

$$\frac{\partial T_2}{\partial x} + \frac{\partial T_1}{\partial y} + \frac{\partial N_3}{\partial z} = 0$$

Since $N_1 = N_2 = T_3 = 0$, these equations reduce to

$$\frac{\partial T_2}{\partial z} = \frac{\partial T_1}{\partial z} = 0$$

and $\frac{\partial T_2}{\partial x} + \frac{\partial T_1}{\partial y} + \frac{\partial N_3}{\partial z} = 0$

Putting the values of T_1 , T_2 , N_3 , we have,

$$\frac{\partial}{\partial z} \left(\mu \left[\frac{\partial \omega}{\partial x} + \frac{\partial u}{\partial z} \right] \right) = 0 \quad \frac{\partial}{\partial z} \left(\mu \left[\frac{\partial \omega}{\partial y} + \frac{\partial v}{\partial z} \right] \right) = 0$$

$$\text{and } \frac{\partial}{\partial x} \left[\mu \left(\frac{\partial \omega}{\partial x} + \frac{\partial u}{\partial z} \right) \right] + \frac{\partial}{\partial y} \left[\left(\mu \frac{\partial \omega}{\partial y} + \frac{\partial v}{\partial z} \right) \right] + \frac{\partial}{\partial z} \left(\lambda \Delta + 2\mu \frac{\partial \omega}{\partial z} \right) = 0$$

These equations reduce to

$$\frac{\partial^2 \omega}{\partial z \partial x} + \frac{\partial^2 u}{\partial z^2} = 0 \quad \frac{\partial^2 \omega}{\partial z \partial y} + \frac{\partial^2 v}{\partial z^2} = 0 \quad . \quad . \quad . \quad (3)$$

$$\text{and } (\lambda + \mu) \frac{\partial \Delta}{\partial z} + \mu \nabla^2 \omega = 0 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Since $\Delta = \frac{\mu}{\lambda + \mu} \frac{\partial \omega}{\partial z}$

$$\therefore (4) \text{ reduces to } \frac{\partial^2 \omega}{\partial x^2} + \nabla^2 \omega = 0$$

$$\text{i.e. } \frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial y^2} + 2 \frac{\partial^2 \omega}{\partial z^2} = 0 \quad (5)$$

$$\therefore \frac{\partial \omega}{\partial x} = \alpha + \beta z \text{ where } \alpha, \beta \text{ are of the first degree in } x \text{ and } y.$$

$$\therefore \omega = \alpha z + \beta \frac{z^2}{2} + F(x, y)$$

But the equation (5) gives,

$$\begin{aligned} \frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial y^2} + 2 \frac{\partial^2 \omega}{\partial z^2} &= 0 \\ \therefore \frac{\partial^2 F}{\partial x^2} + \frac{\partial^2 F}{\partial y^2} + 2\beta &= 0 \quad \therefore \nabla^2 F = A + Bx + Cy \\ &\text{where } A, B, C, \text{ are constants.} \end{aligned}$$

It admits of a solution of the type $F = \Psi + \Omega$

$$\text{where } \Psi = \frac{Ax^2}{2} + \frac{Bxy^2}{2} + \frac{Cyx^2}{2} \text{ and } \nabla^2 \Omega = 0$$

Finally we have from equation (6) $T_1 \sin \phi + T_2 \cos \phi = 0$

$$\left(\frac{\partial \omega}{\partial y} + \frac{\partial v}{\partial z} \right) \sin \phi + \left(\frac{\partial \omega}{\partial x} + \frac{\partial u}{\partial z} \right) \cos \phi = 0$$

$$\text{But } \frac{\partial \omega}{\partial z} \cos \phi + \frac{\partial \omega}{\partial y} \sin \phi = \frac{\partial \omega}{\partial n}$$

where ∂n is the element of the normal

$$\therefore \frac{\partial \omega}{\partial n} + \frac{\partial u}{\partial z} \cos \phi + \frac{\partial v}{\partial z} \sin \phi = 0$$

$$\text{Besides } \omega = \alpha z + \beta \frac{z^2}{2} + \Psi + \Omega.$$

$$\text{Hence we get } \frac{\partial \Omega}{\partial n} = -\frac{\partial}{\partial n} \left[\alpha z + \beta \frac{z^2}{2} \right] - \frac{\partial \Psi}{\partial n} - \frac{\partial u}{\partial z} \cos \phi - \frac{\partial v}{\partial z} \sin \phi.$$

$$\therefore \frac{\partial \Omega}{\partial n} = V(x, y)$$

So, V is known when the right section of the cylinder is given. Ω is therefore a function, such that in the interior of the right section

$\frac{\partial^2 \Omega}{\partial x^2} + \frac{\partial^2 \Omega}{\partial y^2} = 0$ and $\frac{\partial \Omega}{\partial n}$ is the value obtained upon the contour of the same section.

GRAPHICAL REPRESENTATION OF THE TIME OF SUN-RISE AND SUNSET AT ALL PLACES OVER THE EARTH

By

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Complete information regarding the variation in the time of sunrise and sunset at any place on the earth during the course of a year, could be obtained by a graphical representation of the well known equation :

$$\cos H = -\tan \lambda \cdot \tan \delta,$$

where H is the half diurnal circle described by the sun (or any celestial body) over the horizon, λ the latitude of the place of observation and δ the declination of the sun (or of the celestial body).

The diagram is drawn by plotting the values of the full diurnal circle ($2H$ expressed in hours, giving the duration of sunlight), against the declinations $23^\circ 30'$ south to $23^\circ 30'$ north, for different latitudes at intervals of 5° . The local apparent times of sunrise and sunset (expressed in 24 hour system) are also marked on the ordinates at the left and right respectively, in such a way that at a given place, their difference on any particular day is always equal to the value of $2H$. The time of the year corresponding to the solar declination is indicated at the top and bottom of the diagram. In following the variation in the time of sunrise and sunset at a given latitude, one reads from left to right for the months of January to June, and from right to left for the months July to December. To find the local mean time of sunrise or sunset on any particular day, a correction for the equation of time should be applied to the local apparent time. Figure 1 shows the complete chart drawn according to this scheme.

Several interesting features of the diagram may be noted. At the centre, curves for all the latitudes meet, showing that when the sun is on the celestial equator, about the 22nd of March and September, it rises and sets at 6 and 18 hours respectively, at all places on the earth. At the earth's equator there is no change in the time of sunrise or sunset throughout the course of the year, while for places in the northern and southern hemispheres within 30° of the equator, this change is small but it increases rapidly at higher latitudes. The central vertical line for the poles indicates that from the vernal to the

autumnal equinox, the sun is above the horizon at the north pole and below at the south pole, while for the other six months of the year, the reverse is the case. Curves for very high latitudes (beyond 65°) come to an end when the duration of sunlight reaches 24 hours. From this time onwards the sun does not set at these places, till it returns to the same place in the heavens as when the 24 hour day began. Similarly, the period of night for these latitudes is represented by the interval indicated at the other extremities of the curves, showing the duration of sunlight as zero hours.

The diagram shown here is intended to give a general idea of the variation in the length of day and night at different places on the earth at various seasons. In order to read correctly the time of sunrise and sunset, it is obvious that a large scale diagram (about four times the size reproduced here) should be drawn.

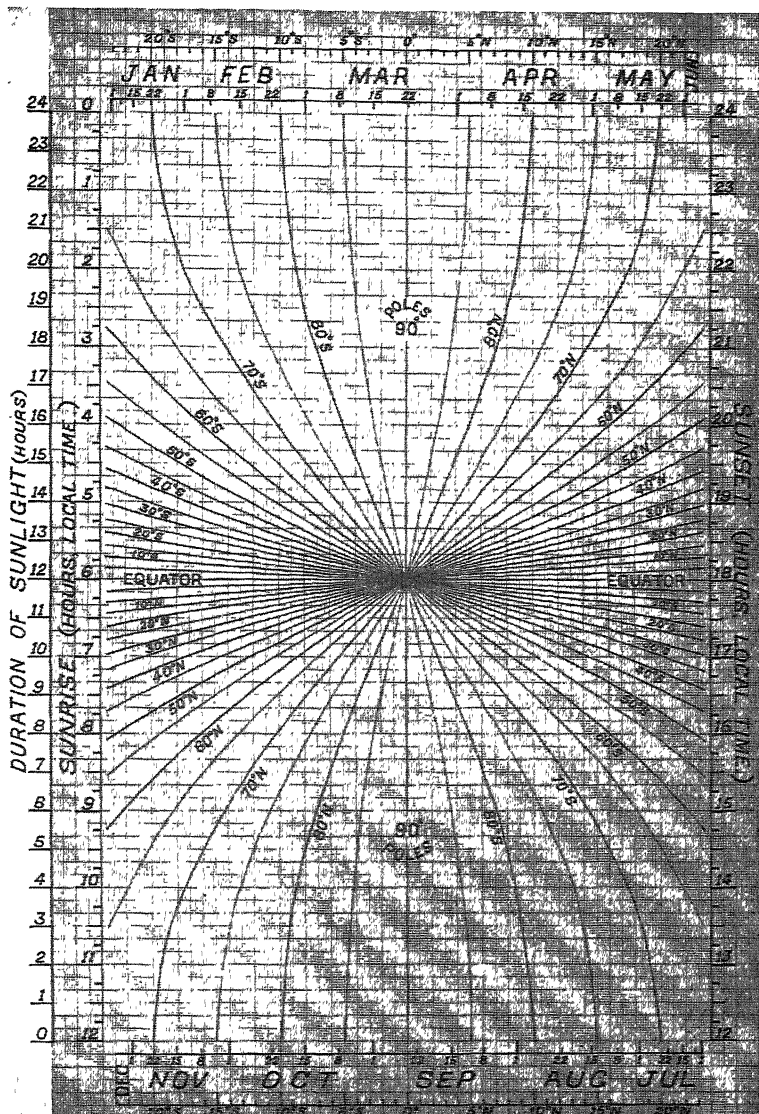


FIG. 1.

THE RECIPROCITY THEOREM IN LIGHT-SCATTERING

By

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The Theorem of Reciprocity is of very wide general application to problems in acoustics and optics, and we owe much to Helmholtz and to the late Lord Rayleigh for putting it on a firm basis. The theorem in acoustics, as also in others, can be stated thus : "If in a space filled with air which is partly bounded by finitely extended fixed bodies and is partly unbounded, sound waves be excited at any point A, the resulting velocity potential ϕ at a second point B is the same both in magnitude and phase as it would have been at A had B been the source of sound." Such a theorem is applicable both to intensity values and velocity potential.

1. IN GASES.

The analogous theorem in light-scattering is due to the late Lord Rayleigh. It can be stated that in all measurements on the scattering of light the intensity of scattered light is the same whether we examine its intensity with a nicol placed with the electric vector vertical in the path of the incident beam or whether we examine its intensity with a nicol similarly oriented in the path of the scattered light. In other words, if we indicate the intensities by V and H for vertical and horizontal components in the scattered track, with sub-letters u , v and h to indicate unpolarised light, vertically polarised and horizontally polarised light (incident beam)—then, it is shown that,

$$V_u = V_v + H_v \quad \dots \quad (1.1)$$

$$\text{i.e. we must have } H_v = V_h \quad \dots \quad (1.2)$$

which proves the theorem of Reciprocity.

In his classical paper on scattering of light by small particles (here molecules), the late Lord Rayleigh derives the intensity for the several cases as given here.

$$V_u = \frac{1}{15} \left\{ 4 (A^2 + B^2 + C^2) + AB + BC + CA \right\} \dots (1.3)$$

$$V_v = \frac{1}{15} \left\{ 3 (A^2 + B^2 + C^2) + 2 (AB + BC + CA) \right\} \dots (1.4)$$

and

$$H_v = \frac{1}{15} \left\{ A^2 + B^2 + C^2 - AB - BC - CA \right\} \dots (1.5)$$

where A, B and C are the optical coefficients dependent on the character of the particle, which are here the optical polarisabilities of the molecules along the three mutually perpendicular axes. It is obvious therefore, that,

$$V_h = H_v$$

This relation has been known to hold true in gases and vapours.

In addition, Lord Rayleigh gives some examples of application in other fields, of which the following may be quoted in his own words :

(1) "Let there be two circuits of insulated wire A and B and in their neighbourhood any combination of wire-circuits or solid conductors in communication with condensers. A periodic electromotive force in the circuit A will give rise to the same current in B as would be excited in A if the electromotive force operated in B."

(2) "From the theory of conduction and radiation of heat, Newton's law of cooling being assumed as the basis, we observe as follows : The temperature at any point A of a conducting and radiating system due to a steady (or harmonic) source of heat at B is the same as the temperature at B due to an equal source at A. Moreover, if at any time the source at B be removed, the whole subsequent course of temperature at A will be the same as it would be at B if the parts of B and A were interchanged."

We shall now consider the applicability of the theorem for scattering in liquid and liquid mixtures.

2. IN LIQUIDS

In liquids, apart from the modified scattering, which is not intense enough to affect the polarisation of the Rayleigh scattering, we can split up the scattered light into two parts, the "density scattering" and the "orientation scattering" or "anisotropic scattering." For liquids with high depolarisation, the scattering is mainly due to orientation scattering. I_a and I_o represent the intensity of scattering due to the first cause and the second cause respectively, and ρ is the depolarisation factor as defined by

$$\frac{\text{Horizontal component}}{\text{Vertical component}}$$

then

$$I_o = I_a \times \frac{6 + 6\rho}{6 - 7\rho} \dots \dots \dots (2.1)$$

We shall now take up the case of a binary liquid mixture, the result of which with a little modification—for the second component is zero—will be valid for a pure liquid.

As shown by Einstein and others, the scattering of a critical solution mixture is made up of three parts, I_d and I_o as defined above, together with I_c the concentration scattering, which is enormous. In fact, Einstein's theory predicts infinite intensity for I_c at the critical solution temperature T_c . It can be easily shown from general considerations that I_c is very great, while I_d comes out usually about $\frac{1}{2}$ to $\frac{1}{4}$ of I_o . If the depolarisation factor ρ is known at T_c , then the total intensity I is given by the relation,

$$I = I_c + I_d + I_o$$

$$= (I_c + I_d) \frac{6 + 6\rho}{6 - 7\rho} \dots\dots\dots (2.2)$$

Moreover, it is well-known that I_c and I_d are completely polarised while I_o is polarised to the extent of $\frac{6}{7}$. With incident vertically polarised light, the factor for I_o is $\frac{3}{4}$. From these we construct the following scheme :

Nature of the incident light Electric vector.	Intensity of the horizontal component in the scattered light	Intensity of the vertical component in the scattered light.	ρ , the depolarisation
Vertical	$\frac{3I_o}{13}$	$I_c + I_d + \frac{4I_o}{13}$	$\frac{\frac{3I_o}{13}}{I_c + I_d + \frac{4I_o}{13}} = \rho_v$
Horizontal ...	$\frac{3I_o}{13}$	$\frac{3I_o}{13}$	1 $= \rho_h$
Unpolarised ...	$\frac{6I_o}{13}$	$I_c + I_d + \frac{7I_o}{13}$	$\frac{\frac{6}{13} I_o}{I_c + I_d + \frac{7I_o}{13}} = \rho_u$

We obtain also

$$\rho_u = \frac{1 + \frac{1}{\rho_h}}{1 + \frac{1}{\rho_v}} = \frac{2}{1 + \frac{1}{\rho_v}} = \frac{2\rho_v}{1 + \rho_v} \dots\dots\dots (2.3)$$

In the above scheme we see that whether we use incident vertically polarised light and observe the total intensity of the scattered light, or use incident unpolarised light and observe only the vertical component in the scattered light, the intensity of the scattered track in both is the same. This is the well-known Reciprocity theorem of Lord Rayleigh.

For pure single liquids, we have to put $I_c = 0$ and re-write all the formula when we get the relationship between ρ_v , ρ_h and ρ_u .

Calculation of intensities :

I_o :—If we know the depolarisation factor ρ_u of the scattered light, by using the formula (2.2) we can easily calculate I_o as a part of the total intensity.

I_d :—In the case of single liquids, if the total intensity of scattered light is I , then I_d is given by

$$I_d = \frac{\pi^2}{2} \cdot \frac{RT\beta}{N\lambda^4} (\mu^2 - 1)^2 \dots \dots \dots (2.4)$$

where μ is the refractive index of the medium.

I_c :—The total intensity of scattering I for all I_c , I_d and I_o , is given by,

$$I = \frac{\pi^2 RT}{2 N \lambda^4} \left[\left(\frac{\partial \epsilon}{\partial k} \right)^2 / m_1 \left(v_2 \frac{\partial p_2}{\partial k} - s_2 \frac{\partial \phi}{\partial k} \right) + \beta d^2 \left(\frac{\partial \epsilon}{\partial d} \right)^2 \right] \frac{6 + 6 \rho}{6 - 7 \rho} \dots \dots (2.5)$$

In the above formula,

k is the concentration defined by $\frac{m_1}{m_2}$ where m_1 and m_2 are the masses of the first and second components respectively.

N is the Avogadro number,

ϵ is the square of the refractive index for the mixture,

p_2 is the partial vapour pressure of the second component,

ϕ is the total vapour pressure,

v is the specific volume of the mixture,

$v_2 \dots \dots \dots$ second component,

β is the isothermal compressibility of the mixture,

R is the gas-constant per gram molecule,

s_2 represents the shrinkages in the volume of the mixture by removal of unit mass of the second component,

and d is the density of the mixture.

It is readily seen that the first term within the brackets represents "concentration scattering" while the second one arises from the "density scattering".

$$\frac{\partial p_2}{\partial k}, \frac{\partial \phi}{\partial k}, \frac{\partial \epsilon}{\partial d} \text{ and } \frac{\partial \epsilon}{\partial k} \text{ can be}$$

readily calculated from experimental data and their evaluations are given in a paper by the author published in the Indian Journal of

Physics (Vol. 8, pp. 280 et seq. 1934). It is needless to repeat them here.

Thus all the different kinds of scattering can be easily calculated from known experimental data.

Using these values for I_e , I_d and I_o one can calculate the theoretical values for ρ_v , ρ_h and ρ_u which can then be compared with experimental data.

This will incidentally verify the validity of the Reciprocity theorem for binary liquid mixtures, for we have taken in the formula that $H_v = V_h$.

August 17, 1936.

ABSTRACTS OF THESES FOR THE M. Sc. DEGREE

I.—*An X-Ray Investigation of the Crystals of p-Nitrobiphenyl and pp'-Hydroazotoluene.* By M. P. LAKHANI, Royal Institute of Science, Bombay.

The crystal structure of the crystals of p-nitrobiphenyl and p-p'-hydroazotoluene have been investigated by the rotation and oscillation method. The dimensions of the unit cell have been found to be

	a	b	c
p-nitrobiphenyl	23.3 Å	11.38 Å	7.54 Å
p-p'-hydroazo- toluene	7.88 Å	7.66 Å	21.66 Å
		$\beta = 90^\circ 11'$	

The crystals of p-nitrobiphenyl belong to the space group Q_h^{15} and have 8 molecules in the unit cell. The crystals of p-p'-hydroazotoluene belong to the space group C_{2h}^5 and have 4 molecules in the unit cell. The molecules in the crystals in both the cases are asymmetric.

M. P.

II.—*Heat of Adsorption of Gases by charcoal.* By S. G. SHARANGAPANI, Gujarat College, Ahmedabad.

The investigation was undertaken with a view to throw light

on the phenomenon of Adsorption in general and that of Chemisorption in particular. Experiments have been conducted with (i) different gases e.g. oxygen, nitric oxide, carbon monoxide, carbon dioxide, nitrogen, nitrous oxide and sulphur dioxide at 0°C . and barometric pressure and (ii) definite volumes of oxygen, nitric oxide and sulphur dioxide at low pressures, on purified sugar charcoal previously exhausted at 900°C . The heats evolved during adsorption were measured by means of Bunsen's Ice Calorimeter and compared with the heats absorbed during desorption of the gases. In all cases, the gases given out on pumping at 0°C , and at 170°C and/or at 900°C were analysed.

The results show that the adsorption of gases such as carbon monoxide, carbon dioxide, nitrogen, nitrous oxide and sulphur dioxide is very much simpler than that of nitric oxide or oxygen, and may be said to be entirely physical in nature. The difference observed in the case of sulphur dioxide from that of carbon monoxide, carbon dioxide, nitrogen and nitrous oxide may be said to be due to the fact that its temperature of liquefaction (-10.1°C)

being very near 0°C , it is held on the surface of charcoal and cannot escape as freely as other gases.

In order to elucidate the process of Chemisorption, experiments were conducted with nitric oxide and charcoal (i) containing fixed oxygen and (ii) containing retained oxygen and nitric oxide. The former was obtained from an experiment with nitric oxide at barometric pressure and at 0°C , followed by evacuation at 170°C , while the latter was obtained from the evacuation of the system at 0°C . This procedure was repeated and the influence of increasing amounts of (i) fixed oxygen and (ii) retained oxygen and nitric oxide on the charcoal surface examined towards the behaviour of nitric oxide.

Attempts have been made to calculate the heats of adsorption per gram molecule (a) of oxygen, nitric oxide, carbon dioxide, carbon monoxide, nitrogen nitrous oxide and sulphur dioxide on the surface of charcoal exhausted at 900°C , and (b) of nitric oxide on the surface of charcoal (i) containing fixed oxygen and (ii) containing retained oxygen and nitric oxide.

On the whole it appears that in the behaviour of oxygen towards charcoal, two processes namely (i) simple adsorption and (ii) sorption of oxygen, are involved, whereas with nitric oxide the process is extremely complicated as the adsorption of nitric oxide is accompanied by (i) the decomposition of nitric oxide, (ii) the

retention of oxygen and of nitric oxide on charcoal and (iii) desorption of nitrogen. With the help of the observations collected in all these experiments the mechanism of the adsorption of nitric oxide is discussed.

V. B. D.

III.—*Anomalous Diamagnetism of Selenium.* By S. S. DHARMATTI, Royal Institute of Science, Bombay.

The diamagnetic susceptibility of selenium decreases as the fineness of selenium powdered in a non-ferrous agate mortar in air is increased and this change is accompanied by the change in the colour of selenium which changes from dark grey first to pink and then to red. The same nature of change in susceptibility is observed when selenium is powdered under paraffin. On washing these powders with alcohol the diamagnetic susceptibility slightly increases but neither the mass value of selenium is reached nor the paramagnetic powders become diamagnetic. On keeping these powders for a long time and on washing them with dilute hydrochloric acid the diamagnetic susceptibility reaches a constant value -0.22×10^{-6} . Also the colloidal selenium prepared by the method of change of solvent in air is paramagnetic but if it is prepared in vacuum it has the same diamagnetic value $-0.22 \times$

10^{-6} . These results show that on powdering and on colloidisation selenium goes over to an allotropic modification, a conclusion which is supported by the calculations made on the basis of Honda and Shimizu's theory.

In the end of the thesis some results are given which show that the effect of light on the susceptibility of selenium is the same as that of light.

M. P.

IV.—*Surface Tension of aqueous solutions of the chlorides of alkaline earth metals.* By C. C. PATEL, Royal Institute of Science, Bombay.

The surface tension has been determined by the method of Fergusson which was improved upon to simplify experimental manipulation to get more accurate values than was possible by the original method. The range of temperatures was from 30° to 60°C with an interval of 5° and that of concentrations from zero to saturation.

It is found that the surface tension increases with concentration but decreases with temperature. The latter change is linear but the former gives curves with slight inflexions in the beginning.

The data obtained have been utilised for calculating surface energy, specific cohesion, adsorption, thickness of the surface layer and Macleod's constant. The parachors of these solutions have

been calculated by the application of the mixture law but it is found that it does not apply in the present case. The parachor of strontium chloride has been predicted from the ratio of the true and calculated parachors of the chlorides of calcium and barium.

S. M. M.

V.—*Physico-chemical studies on solutions of zinc hydroxide in sodium hydroxide.* By M. B. KABADI, Royal Institute of Science, Bombay.

A systematic study of the nature of solutions containing amphoteric oxides and alkali hydroxides has been undertaken at the Royal Institute of Science and attempts are also being made to isolate alkali salts of these oxides in a state of purity. This thesis contains data on solutions of zinc hydroxide in those of sodium hydroxide as well as the details of the isolation of a sodium zincate of definite composition.

Part 1 of the thesis contains results of the measurement of electrical conductivity of solutions containing zinc hydroxide and sodium hydroxide in different proportions expressed as the ratio of ZnO and Na_2O . It is concluded that sodium zincate exists in solutions investigated and that it undergoes hydrolysis when the solutions are diluted. It is suggested that zinc hydroxide may be present as a colloid in dilute solutions.

The results of pH determinations of the solutions used for conductivity measurements are given in Part II of the thesis. The solutions being strongly alkaline the glass electrode was used in these determinations. It is shown that in solutions more concentrated than 6N sodium zincate is hydrolysed only to a small extent.

Part III of the thesis gives the conditions under which a definite zincate of the composition $\text{Na}_2\text{ZnO}_2 \cdot 3\text{H}_2\text{O}$ was isolated.

S. M. M.

VI.—*Properties of aqueous solutions of sodium phosphate.* By S. M. SHETH, Royal Institute of Science, Bombay.

The thesis is divided into three parts. In part I results on the measurement of electrical conductivity at 30°C of solutions containing different ratios of Na_2O and P_2O_5 are given. It is shown that the increase in conductivity on dilution is due to increased ionisation or hydrolysis of sodium salt or salts present in the solution. The equivalent conductivity ratio curves have also been plotted and the change in the direction of these curves is considered to be due to the existence of definite salts in solution.

The details of the construction of a newly designed switch and of the setting up of an electrometer valve unit for the measurement of the hydrogen ion concentration by means of the glass electrode are

described in part II of the thesis. The pH of solutions used in part I was determined and it is shown that the results obtained are in agreement with the conclusions arrived at from the conductivity data.

The third part of the thesis deals with an interesting reaction between solutions of disodium hydrogen phosphate and mercuric chloride. It is shown that the reddish-brown substance obtained by the interaction of the above solutions consists of definite oxychlorides the composition of which depends on the temperature of the reaction. A yellow intermediate substance has been isolated and its composition discussed on the results of analysis.

S. M. M.

VII.—*Studies in Colloidal Prussian blue Hydrosol.* By G. F. MANKODI, Wilson College, Bombay.

The cataphoretic speed of colloidal prussian blue (prepared by peptisation with oxalic acid) with the progress of dialysis first increases and then decreases, while the stability as determined by flocculation values with KCl continuously decreases. The cataphoretic speed on dilution first increases and then decreases in some cases, while it continuously decreases in others; the stability on dilution is found to decrease continuously in all the cases. These results of dialysis and dilution are

exactly similar to those obtained with colloidal ferric hydroxide (Desai and Borkar, Trans. Faraday Soc., 1933, 29, 1269.) and thorium hydroxide (B. N. Desai and A. K. Desai, *ibid.*, 1934, 30, 265.).

The changes in the cataphoretic speed and viscosity under different conditions show that neither the view of Dhar (smaller charge, greater viscosity) nor of Smoluchowski (greater charge, greater viscosity) can individually explain the results.

The idea of critical potential is supported.

The cataphoretic speed of the sol decreases on ageing and exposure to sunlight, sols dialysed for short periods even coagulate when exposed to sunlight for a couple of minutes.

The variation in the conductivity of the sol under different conditions has been studied.

P. M. B.

VIII.—*Studies in colloidal Arsenious sulphide.* BY C. B. JOSHI, Wilson College, Bombay.

The cataphoretic speed of colloidal arsenious sulphide with the progress of dialysis decreases up to 8 days after which it increases till 28 days when it decreases again; the amount of total arsenic and sulphur continuously decreases while that of free arsenious acid increases at first and

then remains constant. The stability with reference to KCl first increases and then decreases, while that with reference to $MgCl_2$ changes exactly as the cataphoretic speed. It is shown that the changes in cataphoretic speed are as a result of changes in the composition of the sol with progress of dialysis.

The changes in the cataphoretic speed on dilution of sol dialysed for different periods are not regular as in the case of colloidal ferric and thorium hydroxides and prussian blue. The stability with reference to KCl and $MgCl_2$ increases regularly on dilution.

The idea of critical potential is not supported in the case of this sol.

The cataphoretic speed decreases generally on ageing and exposure to light; the amount of total arsenic and sulphur (excluding that in the precipitate formed during ageing and exposure to light) decreases, while that of free arsenious acid increases at the same time. The stability with reference to KCl first increases and then decreases, while that with reference to $MgCl_2$ regularly decreases both during ageing and exposure to light.

The variation in the conductivity of the sol under different conditions has also been studied.

It is shown that the results with arsenious sulphide sol should not be utilised either to prove or to disprove any of the existing ideas about coagulation of colloids because changes in the com-

position of the sol introduce considerable complications.

P.M.B.

IX—*Studies in the condition of silver chromate in gelatine and lead iodide in agar and the inhibitive power of agar with reference to lead iodide, lead chromate, silver iodide and silver chromate.* By R. R. KHANOLKAR, Wilson College, Bombay.

Condition of sparingly soluble substance in gels was studied in three parts :—

Part I deals with condition of silver chromate in gelatine. Changes in conductivity and colour of silver chromate in gelatine solution have been studied. It is observed that by suitable adjustment of (i) temperature of the experiment, (ii) pH of the gelatine solution, (iii) concentration of the reactants and (iv) the amount of gelatine, the conductivity may (a) not decrease at all till colour remains yellow, (b) decrease some time after the colour change, or (c) not change at all in spite of colour change.

Part II deals with inhibitive power of agar with reference to some insoluble salts. It is observed that the inhibitive power of agar varies with its pH and is found to be different for different salts.

Part III deals with condition

of lead iodide in agar. Condition of lead iodide in agar is determined by (i) the temperature at which the reaction is allowed to take place, (ii) pH of agar solution, (iii) the amount of agar and (iv) the amount of the reactants.

P. M. B.

X.—*Studies in the properties of Benzopurpurin 4B, Congo Red and Skyblue F.F. under different experimental conditions.* By B. N. ACHARYA, Wilson College, Bombay.

Properties like Surface tension, Viscosity, Conductivity, Stability towards electrolytes and Cathaphoretic speed of Benzopurpurin 4B, Congo Red, and Skyblue F.F. were studied under varying conditions such as with progress of dialysis and dilution and in presence of varying amounts of electrolytes.

Results of the above measurements are embodied in 5 parts of the thesis. In the sixth part the bearing of these results on the mechanism of dyeing is discussed. It is shown that the aggregation of micelles plays a very important part in the mechanism of dyeing cotton by substantive cotton dyes. Success of dyeing depends on suitable adjustments of conditions for getting proper size of the micelles.

P. M. B.

XI.—*Photo-reduction of Ferric Chloride in Alcoholic Solutions.* By B. V. MOHILE, Royal Institute of Science, Bombay.

The reduction of ferric chloride dissolved in various alcohols has been studied in light from a quartz mercury vapour lamp. In dilute solutions the reduction takes place in two stages and in both the stages the order of the reduction is zero molecular. The velocity of reduction changes with the change in the concentration of the ferric chloride solution and nearly obeys the relation

$$-\frac{dc}{dt} = kc^n$$

where n and K are constants for a particular solvent. The temperature coefficient of the reduction is slightly greater than unity. The addition of acetaldehyde to the solutions accelerates the reduction in the early stages.

Some qualitative experiments made to ascertain the mechanism of the photo-reduction of ferric chloride are described in the second part of the thesis. It has been suggested that light activates the ferric ion which breaks up, by collision under favourable circumstances, an alcohol molecule into aldehyde and hydrogen which reduces ferric into ferrous ion. Further it has been found that ferric chloride solutions exposed and unexposed form a photo-voltaic cell the measurement of the E. M. F. of which will lead to the elucidation of the

problem of the photo-reduction of ferric chloride.

M. P.

XII.—*Studies in Thorium Phosphate Gels.* By M. U. PARMAR, Royal Institute of Science, Bombay.

Transparent water clear gels of thorium phosphate have been prepared by using solutions of phosphoric acid instead of those of potassium phosphate and the range of concentrations of thorium nitrate and phosphoric acid which could give clear gels has been determined. The process of gelation is accelerated by the rise in temperature and by an increase in the concentration of the extra electrolytes added to the gel-forming mixtures. The addition of non-electrolytes retards gelation while pyridine precipitates the gel-forming substance. On dehydrating, the gels are reduced to a small mass which when brought in contact with water goes over first to the sol and then to the gel state. This is the first instance in which the phenomenon of reversible sol-gel transformation has been observed in the inorganic gels.

The above mentioned results on the formation of gels and the effect of the addition of electrolytes and non-electrolytes to the gel-forming mixtures have been confirmed by viscosity measurements of these mixtures. These

results have also given some information regarding the rate of the process of gel formation.

The thesis contains in the end two appendices : one dealing with the comparison of the time of set of silicic acid gel-forming mixtures by different methods and the second, with the measurement of the electrical conductivity of the silicic acid gel-forming mixtures during setting.

M. P.

XIII.—A study of the Benzoin Reaction—IV. The Kinetics of the Benzoin Reaction in the Presence of Organic Solvents.

By P. S. REGE, Royal Institute of Science, Bombay.

The object of the present work has been to study the reaction between potassium cyanide and benzaldehyde in the presence of inert organic liquids and of hydroxy compounds. Benzaldehyde was specially purified, and the other materials used were of the highest purity available or suitably purified. The heterogeneous reaction has been shown to be unaffected but the homogeneous reaction is decelerated ; because, a portion of the dissolv-

ed potassium cyanide is precipitated. Hydroxy compounds, on the whole, accelerate the reaction, but their action is complicated.

The time-yield curves obtained with the same quantity of benzene and different amounts of potassium cyanide, were found to be parallel for the autocatalytic portion of the reaction, and increase in the amount of benzene decreased the rate of reaction. The parallel nature of the curves shows, as in the experiments without benzene (Part I, J. Phys. Chem., 1935, 39, 733) that the rate of the autocatalytic reaction is independent of the total quantity of potassium cyanide present and is determined by the quantity of potassium cyanide dissolved in the benzene-benzaldehyde-benzoin mixture.

The equation for calculating the course of the reaction curve for the reaction upto the conversion of about half of the benzaldehyde, which was worked out in Part I, can be applied here using the same value for the heterogeneous constant as previously employed and choosing a smaller value for the homogeneous constant, since a portion of the potassium cyanide has been precipitated. The equation is :—

$$t - c' = 1/k_1 \left\{ \frac{-50}{(10 + X')^2} n' + \frac{(11.51)(30 + 2X')}{(10 + X')^2} \log n' \right. \\ \left. - \frac{(20 + X')^2}{(10 + X')^2} (1.15) \log (10 + X' - n') \right\} \quad (1)$$

or, when X' is small,

$$t - c' = -1/k_1 [-5/n' + 3.45 \log n' - 4.60 \log (10 + X' - n')] \dots (2)$$

where n' = gram. benzaldehyde remaining at time t
 k_1 = the value of the homogeneous constant,
 $X' = 2k_2/k_1$, k_2 being the heterogeneous constant,
 and c' = a constant.

Other inert solvents namely, chlorobenzene, toluene, chlorotoluene, benzyl chloride, cyclohexane, pentane, chloroform, and carbon tetrachloride, give the same type of results as with benzene. The value of the homogeneous constant, k_1 , varies with the solvents. The effect of carbon tetrachloride is greatest; pentane, cyclohexane, and benzene have much the same effect.

Since benzene, not thiophene-free, showed a greater inhibiting effect than the pure benzene employed, the action of thiophene alone was studied. It was found to be an inhibitor of the type studied in Part II (J. Phys. Chem., 1935, 39, 901); very small quantities prove definitely inhibiting. It acts purely on the heterogeneous reaction and the homogeneous reaction is unaffected. Thus a coincidence occurs between curves with a smaller amount of potassium cyanide and potassium cyanide in presence of thiophene. For each of the thiophene curves the equivalent amount of pure potassium cyanide that gives the same results can be found, and hence the amount of potassium cyanide rendered inactive by given amounts of thiophene can be calculated. The curve thus obtained is of the absorption type, the effect of small quantities of thio-

phene being much greater in proportion.

Experiments with acetone showed that it accelerates the benzoin reaction. The accelerated portions of the curves for the same quantity of acetone are parallel, and can be reproduced by equation (2) above by taking the normal value of k_2' , the heterogeneous constant, and an increased value of k_1 which is independent of the amount of potassium cyanide present. The effect of acetone, therefore, would appear to increase the amount of potassium cyanide dissolved in a given mixture of benzaldehyde and benzoin.

Methyl and ethyl alcohols show an accelerating effect on the reaction. The results are, however, complicated, and do not admit of mathematical interpretation. Small quantities accelerate the heterogeneous reaction; intermediate quantities delay the start of the homogeneous catalytic reaction, while larger amounts accelerate the reaction from the beginning. Ethylene glycol gives the same type of results. Polyhydric alcohols increase the rate of reaction even in small amounts. The effect, however, does not increase with the amount of alcohol added, probably because, these alcohols have a very limited solubility in benzaldehyde.

A comparison of the results obtained with the hydroxy compounds shows that glycol and glycerol are more powerful accelerators than methyl and ethyl alcohols. Thus the accelerating effect appears to increase with the number of hydroxy groups in the molecule of the compound added. It should be remembered when discussing the results with hydroxy compounds that they may react with benzaldehyde to form acetyl derivatives.

P. S. R.

XIV.—*A study of the Benzoin Reaction*—V. *The effect of the Inhibitors on the Benzoin Reaction.* By B. F. FARREIRA, Royal Institute of Science, Bombay.

This work comprises a study of the effect of inhibitors on the reaction between pure benzaldehyde and pure solid potassium cyanide. The analytical method and the general technique were as described in Part I of the present series. The inhibitors investigated in the order of the strength are the following :—

Quinone, Iodine, Sulphur, Thiobenzaldehyde, Carbon Disulphide, Selenium and Tellurium. Inhibition can be detected with benzaldehyde containing one part in ten million of quinone.

The similarity of the curves obtained in the presence and absence of inhibitors show that only the heterogeneous reaction is affected. This fact has also been

mathematically confirmed by the following equation :—

$$t - c' = -1/K_1 [-5/n' + 3.45 \log n' - 4.60 \log (10 + X' - n')]]$$

where

n' = gm. benzaldehyde remaining at time t ,

c' = constant of integration, and $X' = 2k_2'/k_1$, k_2' being the heterogeneous constant and k_1 , the homogeneous constant, (See part I J. Phys. Chem. 1935, 39, p. 734)

For the experiments under consideration K^1 remained unchanged and was found to have the value 5.7; k_2' , the velocity constant for the heterogeneous reaction, has the value 0.185 for 1 gm. of effective potassium cyanide per 10 gms. of benzaldehyde. The calculated values agree fairly well with the theoretical values up to about half the conversion of benzaldehyde, when benzoin begins to separate and the equation no longer applies.

It has also been found possible to measure how much solid potassium cyanide is deactivated by an inhibitor in the reaction. The results of the investigations also show that the inhibitor acts by being adsorbed in traces on the surface of the solid potassium cyanide.

By means of adsorption experiments with small quantities of potassium cyanide, it has been found possible to purify various brands of benzaldehyde to a high degree of purity for the benzoin reaction.

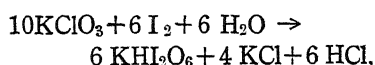
B. F. F.

XV.—*Some Attempts to make out the Mechanism of Chemical Reactions.* BY S. S. DESAI, Gujarat College, Ahmedabad.

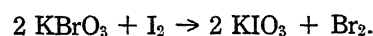
In the present work attempts have been made to throw light on the mechanism of

(i) the interaction between potassium chlorate and iodine, and

(ii) the interaction between potassium bromate and iodine. Under the conditions of the experiment the interaction (i) is found to proceed as



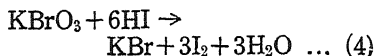
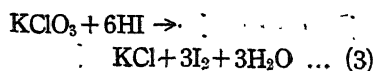
while the interaction (ii) proceeds according to



Although both these interactions at the first sight appear to be different in type, the results clearly show that they are similar and the initial stage involved is the hydrolysis of iodine with water as $\text{I}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HI} + \text{HIO} \dots \dots (1).$

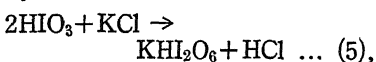
With a rise in temperature hypiodous acid being unstable passes into iodic acid according to $3\text{HIO} \rightarrow 2\text{HI} + \text{HIO}_3 \dots (2),$ and more iodine passes in solution.

In the second stage hydriodic acid produced in (1) and (2) above is oxidised by potassium chlorate and potassium bromate respectively according to the equations



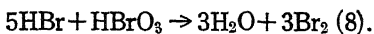
The iodine produced again reacts with water forming hydriodic acid and iodic acid as shown in the first stage and the process continues with the accumulation of iodic acid.

It is in the third stage that the two interactions differ and the difference may be ascribed to the difference in the stability of hydrochloric acid and hydrobromic acid towards chlorate and bromate respectively. In the interaction (1) the accumulated iodic acid in (2) interacts with potassium chloride, in (3) forming potassium biniodate and hydrochloric acid :

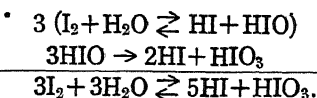


while in the interaction (II), the iodic acid interacts with potassium bromide in (4) as well as with potassium bromate giving potassium iodate according to $\text{HIO}_3 + \text{KBr} \rightarrow \text{KIO}_3 + \text{HBr} \dots (6)$ $\text{HIO}_3 + \text{KBrO}_3 \rightarrow$

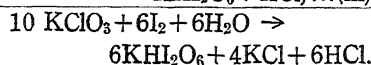
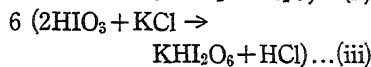
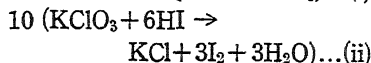
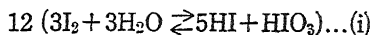
$\text{KIO}_3 + \text{HBrO}_3 \dots (7)$ Hydrochloric acid produced in (5) being stable remains uninfluenced in the process, whereas hydrobromic acid produced in (6) is further oxidised by bromic acid and bromine is evolved :



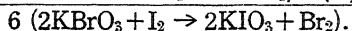
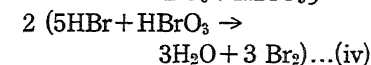
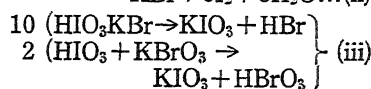
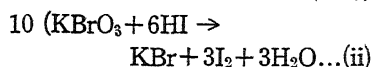
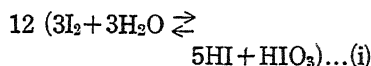
Thus on the whole, the various stages of the interaction (I) and (II) may be summarized as follows :



Interaction I.



Interaction II.



M. S. S.

XVI.—C—Alkyl Resorcinols :—

Part I.—The Chemistry of 4-Ethylresorcinol. Part II.—A New and Direct Synthesis of Rhizonaldehyde. By B. V. SAMANT, Royal Institute of Science, Bombay.

Part I. The Chemistry of 4-Ethylresorcinol :—The discovery of 4-n-hexylresorcinol as a valuable internal urinary antiseptic

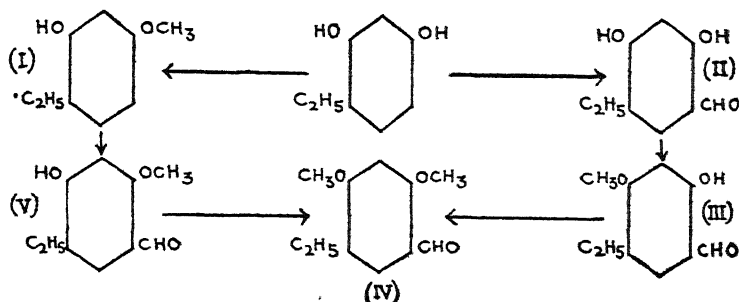
has led a large number of workers to investigate the properties of C-alkylphenols and particularly C-alkylresorcinols.

4-Ethylresorcinol, the most readily accessible of the 4-n-alkylresorcinols, was selected for a systematic study with a view to investigate its chemistry as completely as possible and to prepare compounds from it of possible therapeutic value.

By known methods the following derivatives of 4-ethylresorcinol were prepared :—The diacety-, the di-p-nitrobenzoyl-, and the dibenzoyl esters, the monomethyl and the dimethyl ethers, 2 : 4-dihydroxy-5-ethylphenyl-diazobenzene, 2 : 6-dinitro-4-ethylresorcinol, 2 : 6-dinitroso-4-ethylresorcinol, 3 : 3'-diethylfluorescein, and 2 : 6-dihydroxy-5-ethylphenylarsenic acid.

4-Ethylresorcinol, by the Pechmann reaction, gave the following coumarins :—(i) 6-Ethyl-7-hydroxycoumarin, (ii) 4-methyl-6-ethyl-7-hydroxycoumarin, and (iii) 4-phenyl-6-ethyl-7-hydroxycoumarin.

4-Ethylresorcinol, by the Gattermann reaction, afforded 2 : 4-dihydroxy 5-ethylbenzaldehyde



(II), the constitution of which has been established (Robinson and Shah, J., 1934, 1491). It was characterized by preparing its phenylhydrazone, oxime, semicarbazone, the bromo-, and the acetoxymercury derivatives. It was methylated by the methyl iodide-acetone-potassium carbonate method to give the monomethyl (III) and the dimethyl-(IV) ethers.

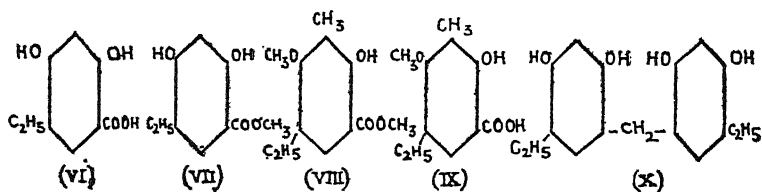
The monomethyl ether (I) of 4-ethylresorcinol gave, by the Gattermann reaction, 2-methoxy-4-hydroxy-5-ethylbenzaldehyde (V) which, on further methylation, gave 2:4-dimethoxy-5-ethylbenzaldehyde (IV). The constitution of the aldehyde (II), the occurrence of the two isomonomethyl ethers (III) and

rylium salt.

By the Knoevenagel reaction, the aldehyde (II), when condensed with malonic and acetoacetic esters gave 3-carbethoxy and 3-acetyl coumarin derivatives respectively.

4-Ethylresorcinol, by the Bistrzycki-Kostanecki reaction gave 2:4-dihydroxy-5-ethylbenzoic acid (VI). It was characterised by preparing its methyl ester (VII) and the bromo derivative. The methyl ester, by the nuclear methylation method of Robinson and Shah (*loc. cit.*), gave methyl 2-hydroxy-3-methyl-4-methoxy-5-ethylbenzoate (VIII), which, on hydrolysis, gave the corresponding carboxylic acid (IX).

Condensation with formal-



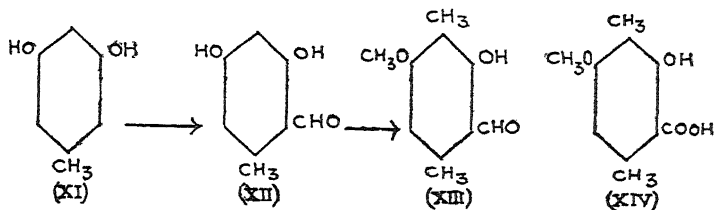
(V) and the cycle of the methylation products obtained, as shown above clearly confirm the constitutions of (I) (III), and (V).

By the Perkin-Robinson reaction, the aldehyde (II) and 5:6-dimethoxy-1-hydrindone gave the characteristic pyrylium salt from which the corresponding free colour base was obtained. The monomethyl ether (III) of the aldehyde (II) and p-methoxyacetophenone, also, gave the corresponding chalcone and the py-

raldehyde in acid medium, gave the methylene compound (X). A number of derivatives were prepared from (X).

These methylene compounds are expected to be very potent bactericides and it is proposed to test them for their antiseptic action.

PART II.—A New and Direct Synthesis of Rhizonaldehyde, 2-Hydroxy-3:6-Dimethyl-4-Methoxybenzaldehyde.



Rhizonaldehyde, related to rhizonic acid, 3 : 6-dimethyl-4-methoxy - 2 - hydroxybenzoic acid (XIV), a degradation product of a number of lichen depsides, like barbatic acid, atranorin, etc., has been an essential intermediate for the synthesis of these complex depsides and related compounds. Its usual synthesis is a long and tedious one, involving a number of stages with diminishing yields. A simple and direct synthesis from orcinol, therefore of rhizonaldehyde, is of great interest.

In the present synthesis, orcinol (XI), by the Gattermann reaction, gave orcyraldehyde (XII), which, by the nuclear methylation method of Robinson and Shah (*loc. cit.*), directly gave rhizonaldehyde (XIII).

R. C. S.

XVII.—Chemical investigation of the constituents of the root bark and seeds of "*Oroxylum Indicum Vent*". By C. R. MEHTA, Royal Institute of Science, Bombay.

PART I.—Constitution of oroxylin-A, a yellow colouring matter isolated from the rootbark

of "*Oroxylum Indicum Vent.*"

Oroxilin was isolated by Naylor and Chaplin ("Year Book of Pharmacy," 1890) from the root bark of *Oroxylum indicum*, Vent, an Indian medicinal plant (natural order Bignoniaceae). Naylor and Dyer (J., 1901, 79, 954) assigned to it the formula $C_{19}H_{14}O_6$ (cf. Warner, Pharm. J., 1898, 7, 390) and inferred the presence of three hydroxyl groups from the preparation of an acetyl derivative which, from the amount of oroxylin it gave on hydrolysis, was assumed to be a triacetate. Hydrolysis with concentrated alkali yielded phthalic and benzoic acids, and a neutral product which gave the pinewood and hydrochloric acid test for phloroglucinol. Dilute alkali produced benzaldehyde, and potassium permanganate, phthalic acid. Methoxy-, carbonyl, and carboxyl groups appeared to be absent.

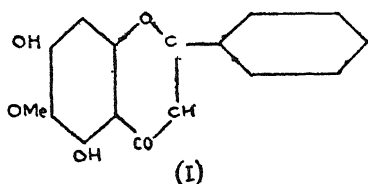
The root bark used in the present investigation was purchased from Ahmednagar Ayurvedashram, or collected from the Songadh forests in Gujarat, and was identified by Dr. K. S. Mhaskar of the Haffkine Institute, Bombay, to whom our thanks are due. We isolated oroxylin by a method similar to that of Naylor and

Dyer (0.2% yield) and also by a new method (0.86% yield). The properties of our products as regards appearance, m.p. analysis, and production of benzoic acid by alkaline hydrolysis agree with those reported by Naylor and Dyer (*loc. cit.*), but in other respects our results are essentially different. On this account, the name oroxylin-A is suggested for our product, although it is probably identical with that of Naylor and Dyer.

Oroxylin-A from its analysis and reactions appears to be a dihydroxy methoxy flavone, $C_{15}H_{12}O_2$ (OH)₂ (OCH₃). It gives a mono—(m.p. 155-156°) and dimethyl ether (m. p. 164-165°), diacetyl (m. p. 131-132°) and monobenzoyl (m. p. 210°) derivatives. Monomethylether platinic chloride (m. p. 185-187°), acetylmonomethyloroxylin-A m.p. 130-131°, benzoylmethyloroxylin-A m.p. 206-208°. Hydrolysis of oroxylin-A and of its monomethyl ether gives benzoic acid indicating the presence of an unsubstituted 2-phenyl group. Demethyloroxylin-A m.p. 265-266° has been shown to be identical with baicalein (5 : 6 : 7-trihydroxyflavone ; mixed melting point—authentic specimen). Further, one hydroxyl group in oroxylin-A is not readily methylated and is feebly acidic indicating that it is in position 5, a deduction confirmed by the positive ferric chloride test. Colour reactions indicate that ortho-related hydroxyl groups are absent. Oroxylin-A is therefore

5 : 7 - dihydroxy - 6 - methoxy flavone, that is, 6-methyl baicalein (I). This conclusion is supported by other considerations.

Monomethyloroxylin-A and dimethyloroxylin-A agree in properties with those recorded for 5 : 6-di-methoxy-7-hydroxy flavone (dimethylether of baicalein) and 5 : 6 : 7-trimethoxy flavone (trimethylether of baicalein) respectively.



PART II.—Composition of the oil from the seeds of “*Oroxylum indicum* Vent” has been investigated. The various constants of the oil have been determined. The acids present are palmitic, shearic, lignoceric, oleic, and probably in a small quantity, an acid higher than lignoceric.

R. C. S.

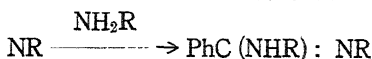
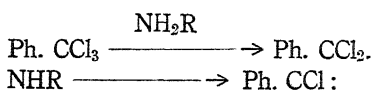
XVIII.—*Studies in the Chemistry of Amidines.* By A.P. KHANOLKAR, Royal Institute of Science, Bombay.

Synthesis of s-Benzenyl-di-phenyl amidines :—

Benzotrichloride has been found to react smoothly with a number of primary aryl amines in presence of nitrobenzene to give corresponding s-benzenyl-di-phenyl amidines in good yields (cf. Lim-

prichet, Annalen, 1865, 135, 82 ; Deobner, Ber. 1882, 15, 233 ; Annalen, 1883, 217, 241).

The reaction in general is presumably as follows :—



Thus it reacts with p- and m-nitranilines and m-toluidine to give s-benzenyl-di-p-nitrophenyl-amidine m.p. 190° ; (hydrochloride sinters at 265°, acetyl derivative m.p. 182-183° and methyl derivative m.p. 188°), s-benzenyl-di-m-nitrophenyl amidine m.p. 147-148° hydrochloride sinters at 275°, sulphate m. p. 196°, acetyl derivative m.p. 135-136°, benzoyl derivative m.p. 195-196° and methyl derivative m.p. 114-115°), and s-benzenyl-di-m-tolyl-amidine m.p. 135° (methyl derivative m.p. 90°).

Oxidation of amidines :—s-Benzenyl-di-phenyl-amidine on treatment with acidic potassium permanganate gives a hydrazine derivative m.p. 112°.

$2\text{Ph. C (: NPh). NPh} \longrightarrow \text{Ph. C (: NPh). NPh. NPh. C (: NPh) Ph. s-Benzenyl-di-p- and m-nitro-phenyl-amidines give hydrazine derivatives m.p. 236° and 262-264° respectively.}$

Condensation of amidines with ethyl chloroformate.—s-Benzenyl-di-m-nitrophenyl-amidine condenses smoothly with ethyl chloroformate to give N-carbethoxy-s-benzenyl-di-m-nitrophenyl amidine, m.p. 153° the structure of

which is confirmed by the fact that it is also obtained by the action of alcohol on the unstable product formed by condensing carbonyl chloride with the amidine. Similar carbethoxy-compounds have been obtained from s-benzenyl-di-p-nitrophenyl-amidine, and s-benzenyl-di-m-tolyl-amidine, and have m.p. 169-170° and 94-95° respectively.

Synthesis of unsymmetrical benzenyl-di-phenylamidines :—For the study of the tautomerism of unsymmetrically substituted benzenyl-amidines, the following have been synthesised by the method of Hill & Cox (J. Amer. Chem. Soc. 1926, 48, 3216) :—Benzenyl-N-p-bromo-phenyl-N'-phenylamidine m.p. 123° (hydrochloride sinters at 265°) ; benzenyl-N-p-nitrophenyl-N'-m-nitrophenylamidine m.p. 170° (hydrochloride sinters at 238°) ; benzenyl-N-p-nitrophenyl-N'-p-tolyl-amidine m.p. 159-160° (hydrochloride sinters at 258°) ; benzenyl-N-p-nitrophenyl-N'-m-4-xylylamidine m.p. 143-144°, (hydrochloride sinters at 237°) ; benzenyl-N'-p-chlorophenyl-N-p-nitrophenyl-amidine m.p. 174-175° (hydrochloride sinters at 272°) ; benzenyl-N'-p-bromophenyl-N-p-nitrophenylamidine m.p. 170-171°, (hydrochloride sinters at 270°) ; p-nitro-benzyl-N-p-nitrophenyl-N'-phenyl-amidine m.p. 230° (hydrochloride sinters at 250°).

On methylation with methyl iodide benzenyl-N-p-bromo-phenyl-N'-phenyl-amidine gives

benzenyl-N-p-bromo-phenyl - N'-phenyl-N-methyl-amidine m. p. 123-124° (picrate m.p. 179-180°) and benzenyl-N'-p-bromo-phenyl-N-phenyl-N-methyl-amidine m.p. 120-121° (picrate m.p. 158-159°).

A. P. K.

XIX.—*Studies in the Chemistry of halogeno amidines.* By S. P. JOSHI, Royal Institute of Science, Bombay.

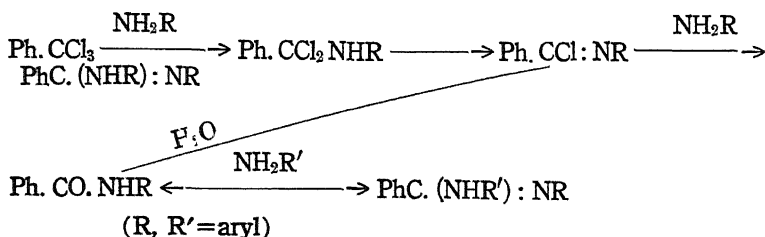
Benzotrichloride has now been found to react smoothly in presence of nitrobenzene with a number of primary arylamines to give the corresponding s-benzenyldi-phenylamidines in good yields (cf. Limpricht, *Annalen*, 1865, 135, 82; Deobner *Ber.*, 1882, 15, 233; *Annalen*, 1883, 217, 241). The reaction probably involves the intermediate formation of a benzanilide-imidochloride for if moisture is present a benzanilide is formed, and further a small yield of unsymmetrical amidine, benzenyl-N-p-chlorophenyl - N'-phenyl-amidine has been obtained from benzo-trichloride, p-chloro-aniline and aniline.

line to give s-benzenyl-di-p-chlorophenylamidine m.p. 143° (hydrochloride chars above 250°, sulphate m.p. 201°, benzoyl derivative m.p. 155-156° and the methyl derivative m.p. 153-154°, the picrate of the methyl derivative m.p. 179-180°), and s-benzenyl-di-s-tribromo-phenylamidine m. p. 196-197° (acetyl derivative m. p. 173-174°, benzoyl derivative m.p. 235-237° and a methyl derivative m. p. 160-161°).

s - Benzenyl-di-p-chlorophenyl-amidine has been found to react with ethyl chloroformate to give N - carbethoxy - s-benzenyl-di-p-chlorophenyl-amidine m. p. 118-119°.

Synthesis of unsymmetrical benzenyl di - phenylamidines :— The following unsymmetrically substituted benzenyl-amidines have been synthesised by the method of Hill & Cox (*loc. cit.*) for a study of the tautomerism.

Benzenyl-N-p-chlorophenyl-N'-phenyl amidine m. p. 120-122° (hydrochloride m. p. 260-262°, benzoyl derivative, m.p. 155-156°); benzenyl - N - p-chlorophenyl-N'-p-methoxy phenyl amidine m. p. 117-119° (hydrochloride m.p. 260°; picrate m. p. 165-



Thus benzotrichloride reacts with p-chloroaniline and s-tribromoani-

166°); benzenyl - N - p-chlorophenyl - N' - p - ethoxyphenyl-

amidine m. p. 95-98° (hydrochloride m. p. 242-244° and picrate m. p. 147-148°); benzenyl-N-p-chlorophenyl - N' - p - tolyl - amidine m. p. 134° (hydrochloride m. p. 283° (decomp.) picrate m. p. 189-190°. Benzenyl - N - p - chloro - phenyl - N' - phenyl - amidine on methylation gives benzenyl - N - p - chlorophenyl - N' - phenyl - N - methyl amidine m.p. 112° (hydrochloride m. p. 226° and picrate 157-158°), and benzenyl - N' - p - chloro - phenyl - N - phenyl - N - p - methylamidine m. p. 102° (picrate m. p. 150-151°). Benzenyl-N-p-chlorophenyl - N' - p - ethoxy - phenyl - amidine on methylation with methyl iodide, gives a mixture of two methyl derivatives m. p. 108° and 89° (picrates m. p. 157-158° and 159-160°).

A. P. K.

XX.—*Studies in the Chemistry of Chalkones and Chalkone-Oxides.* By R. P. DODWAD-MATH, Royal Institute of Science Bombay.

A comparative study of the reactivities of Phenyl-(3. 4-methylene-dioxy-styryl) - ketone (I) and of Phenyl (3. 4-methylene-dioxy-6-nitrostyryl) - ketone (II) has been made. With Br₂ (1 mol) (I) yields CH₂O₂. C₆H₃CHBr-CHBrBz (III), which with Et OH or MeOH gives respectively CH₂O₂. C₆H₃CH (OEt)CHBrBz m.p. 143-44° or CH₂O₂. C₆H₃CH (OMe)-CHBrBz, m.p. 115-116°. With Br₂ (2 mols) (I) yields

CH₂O₂ : C₆H₂Br-CHBr-CHBr-Bz (IV) m.p. 174-75° which is converted into CH₂O₂. C₆H₂Br-CH (OEt)-CHBr-Bz, m. p. 126-27° and CH₂O₂. C₆H₂Br-CH (OMe)-CHBr-Bz, m. p. 131-32°, when boiled with the respective alcohols. On heating (III) and (IV) with KI in CO (Me)₂, the corresponding chalkones, (I) and CH₂O₂ : C₆H₂Br-CH : CH-Bz (V), m. p. 146-47° are formed. (V) is also synthesised from 6-bromo-piperonal and Ac. Ph. Chlorination of (I) with 1 and 2 mols of Cl₂ respectively, gives a pasty mass (which gives on crystallisation from EtOH, CH₂O₂ : C₆H₃-CH (OEt)-CHCl. Bz, m.p. 118-19°), and CH₂O₂. C₆H₂-Cl-CHCl-CHCl-Bz, m. p. 127-28°. With KCN in alcohol, (III) forms CH₂O₂. C₆H₃-CH (CN)-CH₂Bz (V) m. p. 132-33°, hydrolysed to the acid, CH₂O₂. C₆H₃-CH (COOH)-CH₂-Bz (VI), m. p. 143-44°. The structure of (V) and (VI) is confirmed by the similar production of Ph-CH (CN)-CH₂Bz, m.p. 126-27° from PhCHBr - CHBr - Bz and alc. KCN, identical with a specimen obtained by the action HCN on PhCH : CHBz (J. C. S. 1904, 85, (1359). With Br₂ (1 mol), (II) yields CH₂O₂ : C₆H₂ NO₂ CHBr-CHBr-Bz (VII) m. p. 174-75°, reconverted into (II) by treatment with KI in COMe₂, but unreacted with EtOH or with further bromine. (II) with Cl₂ gives the corresponding α-β dichloro-compound m. p. 151-52°. (I) with NaOEt and CH₂

AcCOOEt in EtOH yields *ethyl-2-(3'-4'-methylene-dioxy-phenyl)-4-phenyl- Δ^4 -cyclohexene-6-one-1-carboxylate*, m. p. 151-52°. (II) does not act similarly. (I) is catalytically reduced in presence of palladium to give the corresponding alcohol $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}_2\text{-CH (OH)-Ph}$, m. p. 95-6°, without the formation of the saturated ketone. (II) is not reduced. With $\text{N}_2\text{H}_4\text{H}_2\text{O}$ (I) forms *3-phenyl-5-(3'-4'-methylene-dioxy-phenyl)-pyrazoline*, decomposing on drying; (HCl salt m.p. 197-98; Ac. der. m.p. 153-54°, *picrate*, m. p. 185-186°). With Ph-NH-NH_2 (I) forms *1:3 diphenyl-5-(3'-4'-methylene-dioxy-phenyl)-pyrazoline*, m.p. 129-30°, which gives the pyrazoline reaction and gives a *nitroso derivative*.

Action of H_2O_2 (6%) on (I) in a mixture of MeOH and COMe_2 produces the *oxide of phenyl-(3-4-methylene-dioxy-styryl)-ketone*, (VIII) m. p. 99-100°, which with $\text{N}_2\text{H}_4\text{H}_2\text{O}$ forms a *hydrazone*, m. p. 173-74°, which again with NaOEt or Ac_2O condenses to *3-phenyl-5-(3'-4'-methylene-dioxy-phenyl)-pyrazole* m.p. 194-95°. Treatment of a suspension of (VIII) in MeOH or EtOH with a little H_2SO_4 ruptures the oxide ring with the formation of $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH (OMe)-CH (OH)-Bz}$ (IX) m. p. 117-18° or $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH (OEt)-CH (OH)-Bz}$ m. p. 93-4°. When (IX) is heated with NaOAc-AcOH or with aq. NaOH in alc. solution, or when (VIII) is boiled with aq. NaOH-EtOH, *phenyl-*

(3-4-methylene-dioxy-benzyl)-di-ketone m. p. 114-15° is formed, which with σ -phenylene-diamine yields the *quinoxaline*, m. p. 137-38°. When (VIII) is boiled with aq. NaOH-EtOH for 4 hours, *phenyl-(3-4-methylene-dioxy-benzyl)-glycollic acid*, m. p. 149-50° is formed, which can be readily oxidised by chromic acid to $\text{CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{Bz}$, m. p. 70-71° proving the structure of the acid. (II) is oxidised by H_2O_2 (6%) in COMe_2 to the *oxide of phenyl-(3-4-methylene-dioxy-6-nitro-styryl)-ketone*, (X) m. p. 159-60°; but this is not readily isolated and is better prepared by adding NaOEt to a mixture of $\text{CH}_2\text{Br-CO-Ph}$ and 6-nitropiperonal in EtOH at 0°. Unlike (VIII), (X) does not react with MeOH, EtOH or NaOH, but with HCl-AcOH gives $\text{CH}_2\text{O}_2\text{C}_6\text{H}_2\text{NO}_2\text{-CH (Cl)-CHOH-Bz}$, m. p. 183-84°. With $\text{N}_2\text{H}_4\text{H}_2\text{O}$ in AcOH, (II) gives $\text{CH}_2\text{O}_2\text{C}_6\text{H}_2\text{NO}_2\text{CH : CHCPh : NNHAc}$, m. p. 244-45°, and with PhNHNH_2 , the *phenyl hydrazone* m. p. 159-60 is formed, which is condensed to *1:3 diphenyl-5-(6'-nitro-3'-4'-methylene-dioxy-phenyl)-pyrazoline*, m.p. 203-204° from which AgNO_3 forms the corresponding *pyrazole* m. p. 163-64°, also obtained from (X) and PhNHNH_2 . The results indicate that the nitro group removes the enhanced reactivity which the presence of a nuclear alkoxy group confers on one of the bromine atoms in the chalkone-dibromide; and further it reduces

the reactivity of the oxide towards MeOH, EtOH or alkali, but not towards HCl.

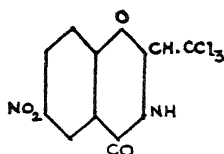
R. P. D.

XXI.—*Studies in Chloralamides.*

By (Miss) K. D. GAVANKAR,
Royal Institute of Science,
Bombay.

Chloral nitro salicylamides and the related compounds are studied in the thesis.

Chloral Amides: These are prepared by nitrating chloral salicylamide and its methyl ether by using various proportions of nitric acid. Thus chloral 3-nitro salicylamide (m. p. 155°), chloral 3 : 5-dinitro salicylamide (m. p. 154°), its methyl ether (m. p. 143°-144°), chloral 5-nitro 2-methoxy benzamide (m. p. 155°) are obtained. Chloral 5-nitro salicylamide and chloral 3-nitro 2-methoxy benzamide are missed by this process. Whereas chloral 3-nitro 2-methoxy benzamide can be obtained by direct condensation; the corresponding chloral 5-nitro compound cannot be obtained by any of these methods. An attempt to condense 5-nitro amide with chloral in a sealed tube gave a closed ring compound (m. p. 201°), a derivative of meta-oxazine series.



from which the following are prepared.

Acetyl derivative (m. p. 176°); α -amino chloral 5-nitro salicylamide (m. p. 146°-148°); α -amino chloral 5-nitro-salicylamide hydrochloride (m. p. 212°-213°); α -amino chloral 5-nitro salicylamide sulphate (m. p. 130°); acetyl derivative of the above α -amino compound (m. p. 180°).

Reactivity of α -OH Group: The following derivatives are prepared:—

(1) Chloral 3-nitro salicylamide:—methyl derivative (m. p. 114°); diacetyl derivative (m. p. 151°-152°).

(2) Chloral 3-nitro 5-bromo salicylamide:—Methyl derivative (m. p. 116°); diacetyl derivative (m. p. 168°).

(3) Chloral 3 : 5-dinitro salicylamide:—methyl derivative (m. p. 172°); dibenzoyl derivative (m. p. 196°).

(4) Chloral 5-nitro 2-methoxy benzamide:—acetyl derivative (m. p. 168°-169°); anhydro derivative (m. p. 207-208°); benzoyl derivative (m. p. 175°-176°); methyl derivative (m. p. 144°).

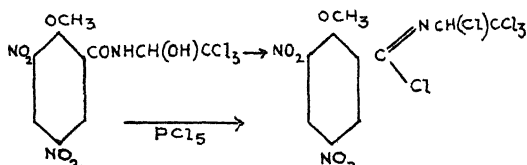
(5) Chloral 3-nitro 2-methoxy benzamide:—methyl derivative (m. p. 87°-88°); anhydro derivative (m. p. 153°-154°); acetyl derivative (m. p. 94°-95°).

(6) Chloral 3 : 5-dinitro 2-methoxy benzamide:—acetyl derivative (m. p. 135°-136°).

Phosphorous pentachloride reacts with the chloral amides producing α -chloro-chloral amides which give further derivatives. Thus chloro-chloral 5-nitro 2-methoxy benzamide (m. p. 149°-

150°) gives :— α -methoxy compound (m. p. 144°); α -ethoxy compound (m. p. 146°-147°); α -(*o*-toluidino) compound (m. p. 151° - 152°); α -(*p*-toluidino) compound (m. p. 171 - 172°); α - anilino compound (m. p. 168° - 169°). α -Methoxy chloral 3-nitro 2- methoxy benzamide (m. p. 104°-105°) is also obtained.

When chloral 3-5-dinitro 2-methoxy benzamide is treated with phosphorous pentachloride it gives an imidochloride (m.p. 91°) which is very stable.



During the course of this work, the various nitro-salicylamides were needed and in order to prepare them the study in the nitro-salicylic acids had to be revised. The following new compounds are prepared.

Methyl 3-nitro 2-methoxy benzoate (m. p. 60°); 3-nitro 2-methoxy benzamide (m. p. 124°); ethyl 5-nitro 2-methoxy benzoate (m. p. 80°-81°); 5-nitro 2- methoxy benzamide (m. p. 213°); ethyl 3 : 5-dinitro salicylate (m. p. 98°-99°); 3 : 5-dinitro salicylamide (m. p. 181°); 3 : 5-dinitro 2-methoxy benzamide (m. p. 166°-167°); 3-nitro 5-bromo salicylamide (m. p. 221°).

N. W. H.

XXII.—Studies in Chloralamides.

By B. V. PATIL, Royal Institute of Science, Bombay.

Monobromination of chloral-salicylamide gave a 5-bromo compound (m.p. 150°-152°) and another product (m. p. 239°) which gives 3-bromo salicylic acid on hydrolysis. Dibromination gave only the 3 : 5 dibromo compound (m.p. 158°-160). Bromination of the methyl ether of chloral salicylamide gives only the 5-isomer (m. p. 147° - 148°) to the entire exclusion of either the 3 or 3 :

5-dibromo compounds.

These bromo - chloralsalicylamides and their methyl ethers have also been obtained by directly condensing their respective amides with chloral. 3 bromo- (m. p. 161°), 3 : 5 dibromo (m. p. 158°-160°)-2-hydroxy - chloral benzamides ; 5 - bromo - (m. p. 147°-148°), 3 : 5 dibromo- (m. p. 156°), 3 bromo- (m. p. 129°)-2-methoxy - chloral-benzamides.)

The α -OH group in the chloral-salicylamides and their methyl ethers has been substituted by groups such as methoxy, acetoxy, benzoyloxy etc. α -Methoxy-chloral-5-bromo-2-methoxy (m. p. 160°), α -benzoyloxy-chloral 5-bromo-2-benzoyloxy (m. p. 97°-

100°), α -acetoxy-chloral-5-bromo-2-acetoxy (m. p. 151°-152°), α -acetoxy chloral-3-bromo-2-acetoxy (m. p. 119°-120°), α -methoxy-chloral-3 : 5-dibromo-2-methoxy (m. p. 108°-109°), α -methoxy-chloral-3 : 5-dibromo-2-hydroxy (m. p. 176°-177°), α -anhydro-chloral - 3 : 5 - dibromo - 2 - acetoxy (m.p. 145°-146°), α -acetoxy-chloral - 3 : 5 - dibromo - 2 - acetoxy (m. p. 155°-157°), α -acetoxy-chloral - 5 - bromo - 2 - methoxy (m. p. 134° - 135°), α -anhydrochloral - 5 - bromo - 2 - methoxy (m. p. 149°-150°), α - acetoxy - chloral 3 : 5 - dibromo - 2 - methoxy (m. p. 117°-119°), α - benzoyloxy - chloral - 3 : 5 - dibromo-2-methoxy (m. p. 124°-126°), α - anhydro - chloral - 3 : 5 - dibromo - 2 - methoxy (m. p. 136°) benzamides.

The α -OH group in the methyl ethers of bromo chloralsalicylamides has been replaced with a halogen atom by reacting with phosphorus halides and the new halogen atom being very reactive, has been replaced by several other groups, in turn. α -chloro-chloral- (m. p. 150°-151°), α -bromo-chloral (m. p. 140°), α -ethoxy-chloral-(m. p. 147°-149°), α -anilinochloral - (m. p. 168°-169°), α - o - toluidino - chloral - (m. p. 166°-167°), α - p - toluidino chloral - (m. p. 175° - 177°), α - phenoxy-chloral-(m.p. 191°-192°) - 5 - bromo - 2 - methoxy - benzamides. 5 bromo - 2 - methoxy-benzoyl - phenylhydrazino (β - trichloro - α - phenylhydrazino - ethyl) - imidine (m. p. 232°), α -

chloro-chloral-(m. p. 109°-110°), α -anilinochloral (m. p. 166° - 167°), α -o-toluidino chloral (m. p. 166° - 167°), α - p - toluidino chloral - (m. p. 173°-174°) - 3 : 5 dibromo - 2 - methoxy - benzamides.

In the end, a general study of bromo salicylic acids and their methyl ethers has been made. In the case of 5-bromo and 3 : 5-dibromo salicylic acids, new methods, that would give pure products, have been worked out. 3-bromosalicylic acid has been produced by a method that gives almost quantitative yields. Moreover, a new general method for methylating bromo salicylic acids with dimethyl sulphate, has been devised. Methyl 3-bromo-salicylate (b.p. 277°-278°); 3-bromosalicylamide (m. p. 162°-163°); ethyl-5-bromo-2-methoxy-benzoate (b. p. 295°); 5-bromo-2-methoxy-benzamide (m.p. 153°-154°); ethyl-3 : 5-dibromo-2-methoxy benzoate (b. p. 305°); 3 : 5- dibromo - 2 - methoxy - benzamide (m. p. 173°-174°); ethyl-3 - bromo - methoxy - benzoate (b. p. 270°) and 3-bromo - 2 - methoxy - benzamide (m. p. 105°-106°).

N. W. H.

XXIII.—*Derivatives of 1-Hydroxy-2-Naphthoic Acid.* By S. N. RAO, Royal Institute of Science, Bombay.

1-hydroxy-2-naphthoic acid, when sulphonated gave 4-sulpho-

1-hydroxy-2-naphthoic acid (König, Ber., 1889, 22, 787; Ber., 1890, 23, 806). The sulpho-acid gave on halogenation (chlorination and bromination) the 4-halogen derivative. The constitution of these compounds is clear since the halogen has substituted the sulphonic group in position 4. The non-entry of the halogen in the side ring is proved by the halogen free phthalic acid that is obtained on oxidation of these halogen acids. Various derivatives of these acids have been prepared.

Derivatives of 4-bromo acid (m.p. $240^{\circ}-1^{\circ}$):—Na salt with $2\frac{1}{2}$ H_2O ; K-salt; phenyl ester (m.p. $104^{\circ}-5^{\circ}$); β -naphthyl ester (m.p. $183^{\circ}-4^{\circ}$); naphthoyl chloride (m.p. $118^{\circ}-9^{\circ}$); methyl ester (m.p. $121^{\circ}-2^{\circ}$); ethyl ester (m.p. $86^{\circ}-7^{\circ}$); anilide (m.p. $164^{\circ}-5^{\circ}$); o-toluidide (m.p. $164^{\circ}-5^{\circ}$); m-toluidide (m.p. $202^{\circ}-3^{\circ}$); p-toluidide (m.p. $150^{\circ}-1^{\circ}$). Derivatives of 4-chloro acid (m.p. $202^{\circ}-3^{\circ}$):—K-salt; phenyl ester (m.p. $103^{\circ}-4^{\circ}$); β -naphthyl ester (m.p. $186^{\circ}-7^{\circ}$); naphthoyl chloride (m.p. $121^{\circ}-2^{\circ}$); methyl ester (m.p. $120^{\circ}-1^{\circ}$); ethyl ester (m.p. $92^{\circ}-30^{\circ}$); anilide (m.p. $180^{\circ}-1^{\circ}$); o-toluidide (m.p. $148^{\circ}-9^{\circ}$); m-toluidide (m.p. $188^{\circ}-9^{\circ}$); p-toluidide (m.p. $143^{\circ}-4^{\circ}$).

Halogenation of 1-methoxy-2-naphthoic acid was carried out and various derivatives studied.

Derivatives of 4-bromo-1-methoxy-2-naphthoic acid (m.p. $196^{\circ}-7^{\circ}$):—phenyl ester (m.p. $88^{\circ}-9^{\circ}$); β -naphthyl ester (m.p. $114^{\circ}-5^{\circ}$); naphthoyl chloride

(m.p. $114^{\circ}-5^{\circ}$); methyl ester (m.p. $96^{\circ}-7^{\circ}$); ethyl ester (m.p. $78^{\circ}-9^{\circ}$); anilide (m.p. $123^{\circ}-4^{\circ}$); o-toluidide (m.p. $142^{\circ}-3^{\circ}$); m-toluidide (m.p. $122^{\circ}-3^{\circ}$); p-toluidide (m.p. $143^{\circ}-4^{\circ}$). Derivatives of 4-chloro-1-methoxy-2-naphthoic acid (m.p. $182^{\circ}-3^{\circ}$):—phenyl ester (m.p. $74^{\circ}-5^{\circ}$); β -naphthyl ester (m.p. $112^{\circ}-13^{\circ}$); naphthoyl chloride (m.p. $106^{\circ}-7^{\circ}$); methyl ester (m.p. $83^{\circ}-4^{\circ}$); ethyl ester (m.p. $77^{\circ}-8^{\circ}$); anilide (m.p. $105^{\circ}-6^{\circ}$); o-toluidide (m.p. $134^{\circ}-5^{\circ}$); m-toluidide (m.p. $116^{\circ}-7^{\circ}$); p-toluidide (m.p. $113^{\circ}-4^{\circ}$).

This study reveals much similarity between the 3-substituted salicylic acids and 1-hydroxy-2-naphthoic acid.

The mode of distribution of bromine between the two nuclei of the arylamides (anilide, toluidides, anisidides and phenetidides) of 1-hydroxy-2-naphthoic acid was studied which is described in detail on page 137.

N. W. H.

XXIV.—*Studies in Chloralamides.* By J. S. DESHPANDE, Royal Institute of Science, Bombay.

The chloralamides of o, m, and p-toluic acids were prepared and studied in this thesis.

Chloral when directly condensed with o, m, and p-tolylamides gave chloral o-tolylamide (m.p. $151^{\circ}-53^{\circ}$), the m compound (m.p. 145°) and the p compound (m.p. $151^{\circ}-2^{\circ}$), respectively.

The reactions of benzoyl chloride, acetic anhydride, and dimethyl sulphate were studied under different conditions, and the following were prepared.

α benzoyl chloral o-tolylamide (m.p. 149°-151°), the m-compound (157°-58°), α acetoxyl chloral o-tolylamide (m.p. 159°-60°), the m compound, (m.p. 142°), and the p compound (m.p. 159°-60°), and α methoxyl chloral o-tolylamide (m.p. 120°-21°).

PCl_5 reacted with the chloral-amides giving α chloro compounds. The o compound (m.p. 172°-73°), the m compound (m.p. 132°-34°) and the p compound (m.p. 111°-12°). These compounds are not very stable and reacted with alcohols, amines, phenols, etc., and the following compounds were obtained.

α methoxyl chloral o-tolylamide (120°-21°), the m compound (m.p. 98°), the compound (m.p. 111°-12°). α ethoxyl chloral o-tolylamide (m.p. 127°-28°), the m-compound (m.p. 145°-146°), and the p compound (m.p. 116°-17°).

α amino chloral o-tolylamide (m.p. 228°-29°), the m compound (m.p. 208°-10°), and the p compound (m.p. 209°-10°).

α anilino chloral o-tolylamide (m.p. 177°), the m compound (m.p. 166°), and the p compound (m.p. 132°).

α methyl-anilino chloral o-tolylamide (135°-36°), α o-anisidino chloral m-tolylamide (m.p. 149°), and α o-phenitidino chloral m-tolylamide (m.p. 145°), α o-tolui-

dino chloral p-tolylamide (m.p. 153°), and α piperidino chloral p-tolylamide (m.p. 132°).

α phenoxy chloral o-tolylamide (m.p. 146°-7°), the m compound (m.p. 140°-41°), and the p compound (129-31°), and α o-cresoloxyl chloral m-tolylamide (m.p. 156°). KCN in excess gave with the m and p chloro compounds, β dichloro α cyano vinyl m-methyl benzamide (m.p. 161°) and the p compound (m.p. 167°), which were hydrolysed by HCl to acids $\text{CH}_3\text{C}_6\text{H}_4\cdot\text{CONHC}(\text{COOH})$: CCl_2 , the m compound (M.P. 189°) and the p compound (M. P. 180°).

N. W. H.

XXV.—*Investigations on the Meteorological conditions in the Air Layers near the ground.* By M. S. KATTI, Indian Meteorological Offices, Poona.

These investigations include a study of the behaviour of soils in different parts of the country when exposed simultaneously to identical weather conditions and also of the physical properties of these soils. The experiments have been conducted during dry months of the year when the surface soil may be so desiccated that it retains only the minimum amount of water.

The following conclusions have been drawn :—

(1) The moisture content of the soil even after intense desic-

cation at depths of 1 ft. is as high as 30%.

(2) At the epoch of maximum temperature, decrease of water contents of air layers at a height of 10 ft. above the ground is on the average 25% of the mean value for the 10 ft. layer. At the epoch of minimum temperature, the conditions are reversed so far as the pressure of water vapour is concerned.

(3) Daily measurements of the moisture content of soil samples showed that the soil has much more moisture in the morning than in the afternoon.

(4) Hourly determinations indicated that the soils have their minimum moisture content at the epoch of maximum temperature and maximum moisture content

at the epoch of minimum temperature.

(5) The water-holding capacities or moisture-variation-indexes of soils at Poona, Sholapur, Hagar, Bangalore, Pusa and Lylapur have been found. The results show that black cotton group of soils is able to retain 15% more of water than alluvial group. The values of the heat of wetting run parallel to those of the moisture-variation-index.

(6) Comparison of the desiccating power of different soils revealed that Poona soil retains its power to absorb for the longest time, the next in order being Jalgaon, Bangalore and Lylapur. The results suggest that black cotton soils may be used with profit for keeping the air in an enclosed space dry.

N. R. T.

REVIEWS

An Introduction to Projective Geometry. By Dr. L. N. G. FILON, D.S.C., F.R.S. Fourth Edition, pp. xviii + 407. (London, Edward Arnold & Co. 1935, 16|- net.).

This is the latest edition of a well-known book by a well-known author. It differs considerably from the previous editions having been thoroughly revised and contains many new additions. The general scheme of the book, however, remains unaltered.

In the first eight chapters of the book (including one on involution), the author has confined himself to accessible and real elements to give familiarity and confidence to the beginner. In Chapter IX, imaginary elements and the circular points at infinity are introduced by an appeal to algebraic considerations. This is followed by seven chapters on homography, reciprocation and inversion, systems of conics, projective methods in three dimensions and further properties of quadrics.

This edition like the previous ones contains a large number of exercises in practical drawing; this may not appeal to some students of Mathematics but it is nevertheless a valuable feature of the book. Other noteworthy features are a new treatment of the circle of curvature based upon the projective transformation of conics having three-point and four-point contact, some results on the curvature of twisted curves and of quadrics; an introduction to the general plane cubic and quartic obtained from pencils of conics and so on.

The book will be found to be very valuable by students of Geometry and may be commended to the notice of B.A. and M.A. students of this University. The printing, figures and general get-up are all excellent. The price 16|- net is somewhat beyond the reach of most students in India and we hope that it can be reduced to a more reasonable figure.

K. R. G.

Fuel. By J. S. S. BRAME and J. G. KING. 4th Edition, 1935. (Edward Arnold & Co. London. 25|-).

The fourth edition of this work is a considerable enlargement of the previous volume; the subject matter has been brought up to date

and a considerable amount of new material has been introduced. The volume deals with latest methods for the production, refining and scientific utilisation of the various solid, liquid and gaseous fuels. Critical surveys of the different processes involved, discussions on the efficient and economic utilisation of all types of fuels, and future prospects for natural, synthetic and mixed fuels as materials for the production of power and heat are given ; and these add greatly to the value of the work containing condensed information on almost every type of present day materials used as domestic and industrial fuels.

Dr. J. G. King of the Fuel Research Station, Greenwich (D. S. I. R.) by his collaboration in the production of this edition, has added materially to the usefulness of this work. The chapters on the low temperature carbonisation and hydrogenation of coal are, for example, a welcome addition ; especially at present, when most of the countries lacking in natural oil resources are installing suitable plants to ensure emergency supply of synthetic petrols. I. C. I. Ltd. have recently put up a huge plant at Billingham in England which is now in operation, while I. G. have already established this industry in Germany on a large scale. Final chapters devoted to the analysis of fuels briefly survey the tests for their relative merits ; few details are given regarding the individual tests. Chapter on Calorimetry, however, is very comprehensive and deals exhaustively with this part of the subject.

The book is clearly written, well printed and produced. References to the literature are insufficient, and the usefulness of the book would be enhanced by the inclusion of a bibliography at the end of every chapter. The work is a sound contribution to the Technology of Fuel, and the information given therein may be depended upon as thoroughly reliable.

L. A. B.

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Relativity, by F. W. Lanchester, (Constable) London, 1935.

Junior Trigonometry for Colleges, by L. S. Patrachari and S. A. Mani, Longmans, Bombay, 1936.

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EXCHANGES

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* * Only No. 5.

* Only Nos. 1, 4 and 5.

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The Curator, Oriental Mss. Publication Department, Trivandrum (Travancore).

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* Part V for abstracting purpose only.

Journal OF THE University of Bombay



[BIOLOGICAL SCIENCES INCLUDING MEDICINE: No. 5]

Vol. V

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PUBLISHED

FOR THE

UNIVERSITY OF BOMBAY

BY

LONGMANS, GREEN AND CO. LTD.

53 Nicol Road,
BOMBAY

6 Old Court House Street,
CALCUTTA

36A Mount Road,
MADRAS

LONDON : NEW YORK : TORONTO

JOURNAL OF THE UNIVERSITY OF BOMBAY



This journal is mainly intended to promote research work by the teachers and students of the University of Bombay. It will contain original articles, abstracts of theses and reviews of books, and will be issued six times a year, the issues being devoted to the following subjects in their order :—

- No. 1. *History, Economics and Sociology.* (July)
No. 2. *Physical Sciences, including Mathematics.* (September)
No. 3. *Arts and Law.* (November)
No. 4. *History, Economics and Sociology.* (January)
No. 5. *Biological Sciences, including Medicine.* (March)
No. 6. *Arts and Law.* (May)

RATES OF SUBSCRIPTION

Annual Subscription for six issues.	Rs. 14 -
„ „ „ Nos. 1 and 4 „	5 -
„ „ „ „ 2 „ 5 „	5 -
„ „ „ „ 3 „ 6 „	5 -
Single Copy	3 -

(Inland Postage Free)

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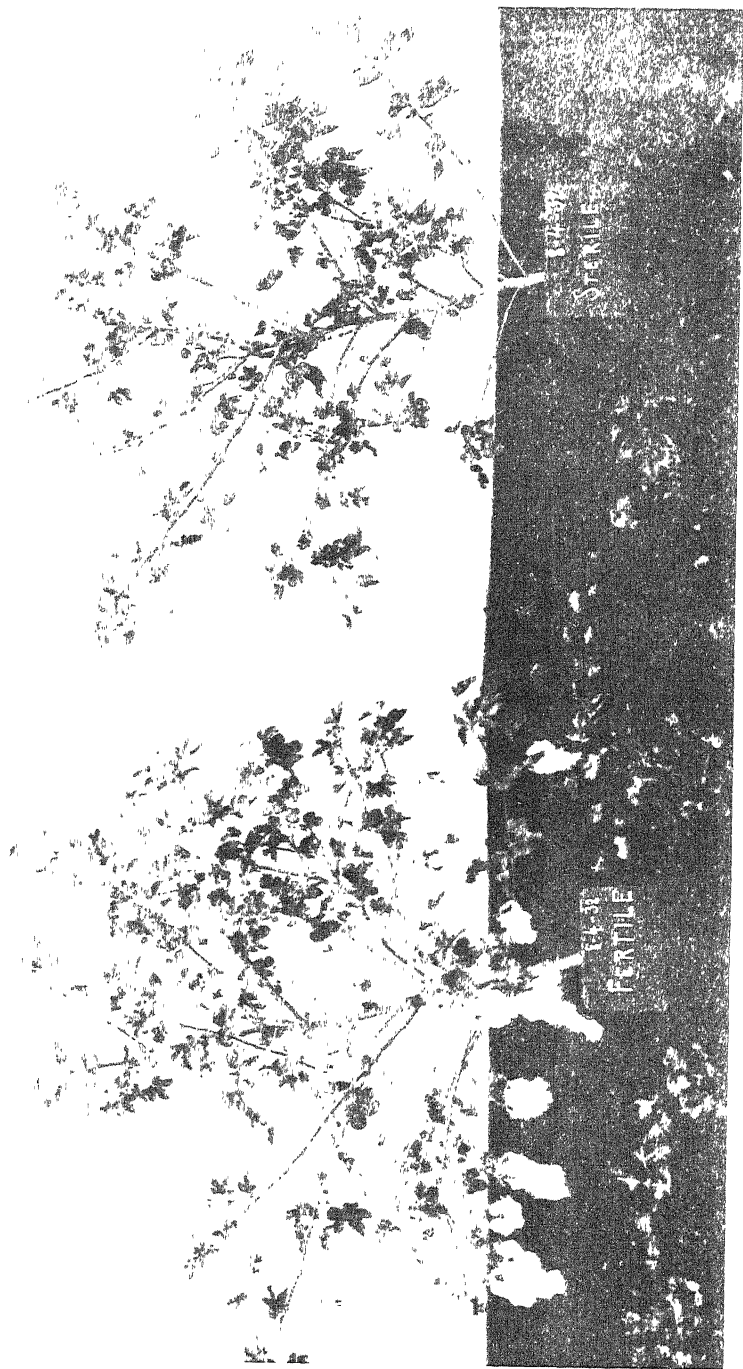


FIG 1. The fertile and the sterile plants of the 1027 A.L.F. cotton growing at the Agricultural Experimental Station, Surat.

Journal OF THE University of Bombay

[BIOLOGICAL SCIENCES, INCLUDING MEDICINE : No. 5.]

VOL. V

MARCH 1937

PART V

STERILITY IN COTTON

By

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CONTENTS

- I. Introduction.
- II. Material and Method.
- III. Pollen Study ; (a) Pollen size ; (b) Pollen viability ;
(i) Iodine reaction method ; (ii) Pollen germination ;
(c) Abnormal pollen.
- IV. Cytological Study : (a) Resting nucleus ; (b) Prophase ;
(c) Metaphase , (d) Anaphase ; (e) Telophase ; (f) Size
of chromosomes ; (g) Abnormalities of other types.
- V. Discussion.
- VI. Summary.
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I. *Introduction.*

The incidence of sterility both in plants and animals has been observed from very long times. The exact causes leading to sterility may be either morphological, physiological or genetic. It may be the result of any of these causes operating severally or collectively. When none of the above causes are operative some alteration in the

chromosomal complex will lead to an abnormality such as partial or complete sterility.

The practical utility of the result of investigations into sterility in plants is well instanced in the case of bearing in commercial fruit crops, particularly those of apples, pears, plums, cherries, strawberries, etc., grown extensively in Europe and America. Many varieties of these fruit trees of commercial importance were found either to be extremely shy bearers or would bear no fruit at all. On investigation it was found that the cause of this was self-sterility which was due to incomplete or complete non-functioning of the male gametes. Self-sterility was found to vary according to variety and ranged from complete to partial self-sterility. The selection of varieties for use as "pollinators" for growing in orchards planted with varieties which were self-sterile, has completely overcome the problem of bearing in these fruit crops.

Sterility in fruit crops has been investigated into among others by Chittenden³ and Crane⁶ in England, Connors⁵, Longley¹⁵, Darrow⁷, Beal¹ and Clark⁴ in U.S.A., Florin⁸ in Sweden, Pashkevitch¹⁶ in Russia. Harrison and Blackburn¹¹ have worked on pollen sterility in roses, Shull¹⁷ in shepherd's purse, Jones¹³ in maize, and Clark⁴ in potato.

Longley¹⁵ found that, in *Rubus*, evenly balanced forms such as the diploid, tetraploid, hexaploid, and octoploids produced fertile pollen while triploid and pentaploid forms produced sterile pollen in abundance with very little fertile ones. In *Datura*, Blakeslee and Cartledge² observed that the aborted pollen grains were chiefly brought about by chromosomal deficiencies and according to them, the higher percentage of non-disjunction in primaries is believed to be responsible for the higher percentage of bad pollen in primaries compared with the diploids. Shull¹⁷ observed that sterility in shepherd's purse was due to a gene recessive to normal pollen-fertility. In the majority of instances sterility in plants is limited to either the male or female sex and seldom it affects both. Complete sterility both on the male and the female side is often met with in polyploids and heteroploids or in hybrids from wide crosses between distantly related species or genera. The interspecific crosses between the old and new world cottons have invariably resulted in a sterile hybrid. Harland⁹ was the first to raise an F_2 and subsequent generations from an American \times Asiatic cotton cross by obtaining a few functional pollen of the hybrid and using them in back-crossing to the American parent. A similar attempt by Kanash¹⁴ to obtain fertile progeny between the old and new world cottons was successful and he found that the F_1 hybrids were not completely

sterile and by repeated back-crossing he carried forward the progeny upto F_3 generation. Kanash was of the opinion that interspecific hybridization between the 52 and 26 chromosome types of cotton did not result in entire sterility of the F_1 hybrid. In heteroploids sterility is the result of unbalanced nature of the chromosomes and unequal distribution in their number at the time of meiosis, during gametogenesis.

While references to the work on sterility in malvaceous plants are available, reference to published work explaining the causes of sterility in cotton is scanty. Harland¹⁰ refers to a "Man Cotton" which on cytological examination by Skovsted was shown to be a haploid. Haploidy then was the cause of male sterility in *G. Barbardense* var. *maritima*. Two instances of heritable types of sterility in cotton are reported. Hutchinson and Gadkari¹² found that in "Million Dollar" cotton the sterility was equal on male and female side and it was inherited on a monogenic basis. Vijayaraghavan *et. al.*¹⁸ report of an instance of female sterility in a pure strain (No. 1281) of *G. herbaceum* which was inherited according to monofactorial ratio. In both these instances the normal fertile type was dominant to the sterile.

The present paper throws some light on the sudden occurrence of complete sterility in a *herbaceum* (1027 A.L.F. Gujarath) cotton and the causes leading thereto.

II. Material and Method.

The attention of the writer was first drawn to the occurrence of about half a dozen sterile cotton plants on the Government Farm at Surat in 1932 by Mr. K. V. Joshi, the then Cotton Physiologist. These plants appeared among those on which he was carrying out physiological experiments. The sterile plants are from the cotton variety 1027 A.L.F. (*G. herbaceum*), a superior type cultivated extensively south of the Narbuda river in Gujarat in the Bombay Presidency and highly valued for its superior staple.

A close comparison between the fertile and sterile plants of this variety of cotton showed that there was no difference in any of their morphological characters. The habit of the fertile and the sterile plants, the time, duration and extent of flowering were alike in both. Even with regard to the opening of flowers and anthesis the sterile plant conformed to the fertile type. Under field conditions the only difference by which these two types could be differentiated

was in regard to the setting of bolls. While the fertile type set the normal number, the sterile failed to set a single boll (Fig. 1). The study of the pollen of the two types revealed that there was considerable difference between them in respect of size, iodine reaction and germinability. From a few preliminary trials it became apparent that the cause of sterility was due to some aberration in the chromosome complex of the germinal material. The flower buds of the sterile plant were fixed *in situ* at Government Farm, Surat, in 1932. A layered plant of the sterile type was brought to Poona during the same year and has been kept under observation since then.¹

For cytological study, the microsporogenous material was fixed in Bouin's fluid and embedded in paraffin. The sections were cut from 8 and 10 μ thick and stained with Delafield's Iron-alum Hæmatoxylin. Before the anthers of a flower bud were fixed a few were taken out and crushed in a drop of water on a slide and were examined under a microscope to find out whether the stage of development of the pollen mother cells was such as to include one or the other of the stages of nuclear division under study. The anthers of buds whose stage of microspore development was either too early or too advance were rejected. From this preliminary examination it was possible to associate a certain stage of development of the pollen mother cells with a definite phase in nuclear division. The existence of such a relationship considerably saved time and material, and helped to avoid embedding, cutting and staining the several hundred buds before those which were useful for purposes of investigation could be retained.² The young buds were collected in bright sunshine when division was at its maximum i.e. between 10 A.M. and 2 P.M. The figures were drawn with the aid of a Camera Lucida.

III. Pollen Study.

(a) *Pollen Size* :—The most noticeable difference between the fertile and sterile types was in regard to the size of their pollen as shown in the table below.

1. Examination of the material periodically fixed from the layered plant at Poona has shown the presence of the same types of irregularities that were observed in the pollen mother cells fixed *in situ* from plants at Surat.

2 Permanent preparations of the pollen mother cells of the sterile plant prepared according to a modified smear method were also examined along with sections cut from the material embedded in paraffin. Excellent preparations were obtained from material embedded in paraffin and those prepared by smear method.

TABLE I. *The frequency in pollen size of the sterile and the fertile types of 1027 A.L.F. Cotton.*

Diameter in μ	Type of Plant	
	Sterile	Fertile
16	1	.
20	3	.
24	28	.
28	.	.
32	31	2
36	3	.
40	29	6
44	11	.
48	67	20
52	46	6
56	69	72
60	59	19
64	217	335
68	47	30
72	43	9
76	15	1
80	58	.
84	17	.
88	20	.
92	8	.
96	15	.
100	8	.
104	2	.
108	4	.
112	1	.
Total	700	500

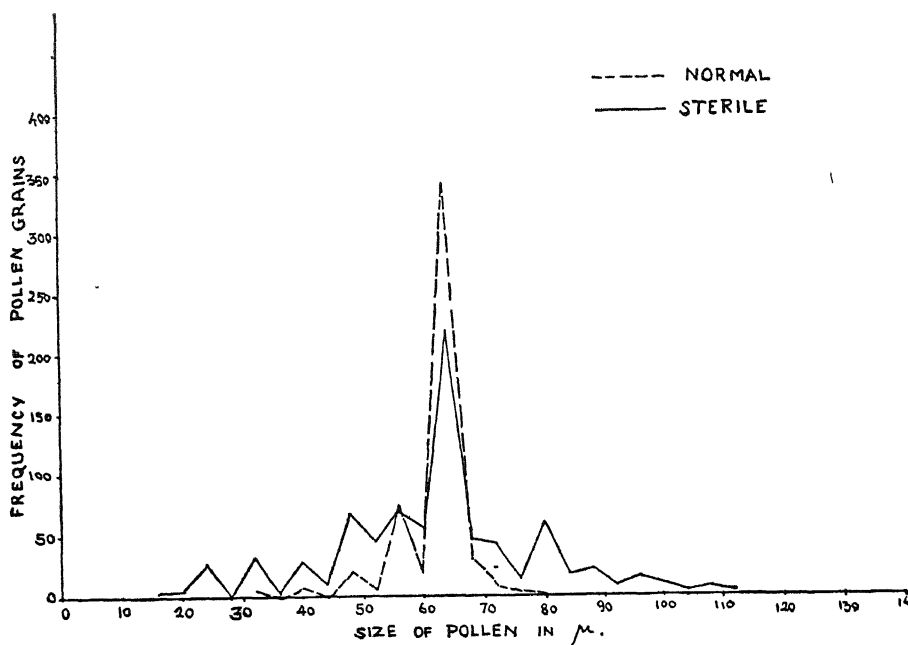


Fig. 2. Frequency curves of pollen size of the sterile and the fertile types of the 1027 A.L.F. cotton.

Table I and Figure 2 show that while the mode is the same for size of pollen of the sterile and the fertile types, there is considerable difference not only in the range of variation but also in the frequency. The size of the pollen of the sterile varied from as small as 16μ to as large as 112μ , while the smallest pollen of the fertile is only 32μ and the largest no bigger than 76μ . In respect of frequency the sterile type showed 31 per cent. falling in the modal class while the value for the fertile type is as high as 67 per cent. It will later be seen that there is a correlation between the size of the pollen and its chromosome number, in the sterile type (p. 12). The larger have more and the smaller less than the haploid number of chromosomes.

(b) *Pollen Viability* :—The viability and functioning of pollen was tested by two methods, viz., (i) iodine reaction method for abortive pollen and (ii) germination trials.

(i) *Iodine reaction method* : The iodine method gives an indication of the percentages of aborted or empty pollen and those which have the protoplasmic contents intact. In the case of the fertile plant out of a total of 200 pollen tested, it was found that 80.5 per cent. stained deep blue with iodine while 19.5 per cent. were empty and re-

mained unstained. Exactly reverse was the case with the sterile type in which the percentage of abortive pollen was as high as 79.0 and the remaining 21.0 had the protoplasmic content intact.

(ii) *Pollen germination* :—The germination of pollen of cotton cannot easily be brought about because of the high osmotic concentration of the sap of the microspore. Therefore, when the microspores are placed in water rapid diffusion takes place with consequent bursting of the spores. Satisfactory germination could be obtained by using cane-sugar solution whose concentration had to be as high as 40 per cent. When the pollen grains of the sterile and fertile types were placed in such a sugar solution it was observed that while there was good germination in the case of the pollen of the fertile type those of the sterile totally failed to develop the pollen tube. In order to induce germination under a more natural environment flowers of both types in which the anthers had not dehisced and which were emasculated, were placed in separate culture jars with their stalks dipping in water. To the stigmas of flowers of each of these types the pollen grains of the opposite type were applied by a camel hair brush. The results are given in Table II.

TABLE II. *Germination trials of pollen of sterile and fertile cotton types (i) in sugar solution and (ii) on stigmatic surface.*

Type of pollen.	Germination		
	in 40% sugar solution.	When applied to stigmatic surface	
		Stigma of fertile flower.	sterile flower. Stigma of
Fertile	+	+ ¹	—
Sterile	—	—	—

It will be observed that the sterile plant is sterile both on its male as well as female side since its own pollen fails to bring about self-fertilization or effect cross-fertilization when used on a fertile plant. This was further corroborated by numerous crosses that were effected between the sterile type and several fertile cotton

¹ Control—pollen of fertile plant used on stigma of its own flower.

varieties and their reciprocal crosses. Species of *Gossypium*, viz., *indicum*, *neglectum* and *herbaceum*, were used for testing the fertility of the male and female gametes of the sterile type and in not a single instance did these crosses set a single boll, definitely indicating that gametes of both the sexes were sterile. In the case of controls where a fertile type was crossed with another fertile type bolls were easily obtained. Further similar germination trials were also made with the pollen of the sterile type which by the iodine test was found to have their protoplasmic contents intact. Even in these development of the pollen tube did not take place in a single case showing that a sterility factor is affecting them.

(c) *Abnormal pollen* :—In yet another respect the sterile and the fertile types differ very markedly in the formation of the tetrads from the pollen mother cell. In the normal type each pollen mother cell gives rise to a group of four or tetrad of pollen and it is extremely rarely that the pollen mother cell divides to produce more than four microspores. The tetrads normally produced are uniform in size and shape. Examination of the pollen mother cells of the sterile plant showed, however, that they frequently gave rise to more than four microspores of varying sizes, sometimes as many as ten (Plate V, Fig. 29.) The variation from the normal is given in Table III.

TABLE III. *Frequency of pollen mother cells producing abnormal number of microspores in the fertile and the sterile 1027 A.L.F. cotton.*

Type of plant.	Frequency of microspores.											Total.
	1	2	3	4 ¹	4 ²	5	6	7	8	9	10	
Fertile	489	...	6	3	2	500
Sterile	49	11	249	76	63	41	8	1	2	...	500

From the above it is clear that in the fertile plant the percentage of pollen mother cells which produce an abnormal number of microspores is only 2.5 while in the sterile plant it is as high as 50. Of the remaining 50 per cent. majority are abortive or empty while some have the protoplasmic content. Even these few are non-functional due to their being affected by sterility.

¹ Tetrads classed as normal because of their uniform size and shape.

² Tetrads classed as abnormal because of the difference in their size and shape.

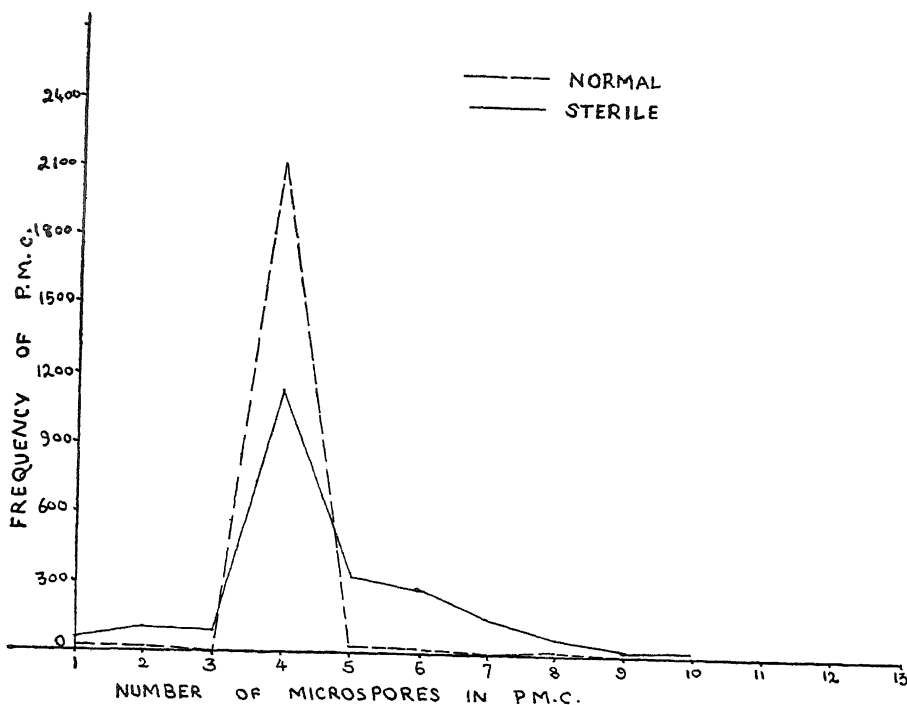


FIG. 3: Frequency curves of pollen mother cells producing abnormal number of microspores in the fertile and the sterile 1027 A.L.F. cotton.

The above frequency curve of pollen mother cells producing abnormal number of microspores in the fertile and the sterile 1027 A.L.F. cotton shows the wide divergence between the two. In the fertile the number of pollen mother cells producing microspores either less or more than four is 56 out of a total of 215 cells counted or approximately 2.5 per cent. while in the sterile the percentage of abnormal was found to be 48.5 i.e. nearly twenty times as great.

Further a comparative study was made in fourteen different varieties of normal fertile cotton for the abnormally produced microspores and is given in Table IV.

TABLE IV. *Frequency of pollen mother cells producing abnormal number of microspores in different varieties of cotton.*

No.	Name of variety.	1	2	3	4	5	6	7	8	9	10	Total
1	1027 A. L. F. Sterile	47	109	88	1134	316	283	138	60	12	3	2185
2	1027 A. L. F. Fertile	26	6	0	2102	18	3	1	2	0	0	2159
3	Bani	0	3	3	232	0	0	0	0	0	0	238
4	Banilla	3	3	6	370	0	0	0	0	0	0	382
5	Wagale	8	3	1	230	0	0	0	0	0	0	242
6	Dharwar-American	18	1	0	284	0	0	0	0	0	0	303
7	Dharwar No. 1	1	0	2	239	0	0	0	0	0	0	242
8	Jaywant	1	0	1	244	4	0	0	0	0	0	250
9	Comilla	9	2	0	234	0	0	0	0	0	0	245
10	No-lint	1	3	0	210	0	0	0	0	0	0	214
11	N. R. 6	12	0	0	204	0	0	0	0	0	0	216
12	1-A. Long Boll	0	1	0	230	0	1	0	0	0	0	232
13	Wagad	1	0	0	203	2	1	0	0	0	0	208
14	Gadag. 1	0	3	1	207	1	2	2	0	1	0	217

From a perusal of Table IV it becomes clear that in twelve varieties of cotton other than 1027 A.L.F. the percentage of pollen mother cells which produce more than four microspores is less than two. Even with respect to the production of microspores less than four in number by pollen mother cells which is commonly met with in all varieties and which is the result of arrested development, the sterile 1027 A.L.F. type far exceeds the proportion normal to fertile types of all varieties of cotton.

It will later be evident that these extra microspores are produced due to onset of more than two nuclear divisions (p. 12) while two is the normal number to give rise to the tetrad. The further sub-division of the cytoplasmic and nuclear material usually meant for the production of four microspores results in the formation of abnormal types with unbalanced number in respect of chromosomes and inequality in cytoplasmic contents. The microspores produced as a result of more nuclear divisions are either smaller or larger in size as compared with the normal spore and these fail to germinate and produce the pollen tube even when their

protoplasmic contents are present and appropriate conditions are available. It is clearly seen that in the sterile 1027 A. L. F. Cotton abnormally produced microspores, presence of abortive pollen, and sterility of those that appear to be normal are the three contributory causes which result in cent per cent sterility of the pollens.

IV. *Cytological Study.*

In this, particular attention was paid to the types of abnormalities which occur at the time of meiotic division during gametogenesis in the sterile plants. A comparison of the different stages of nuclear division at the time of the formation of the male gametes of the sterile and the fertile types was made to study the deviation from the normal that occur in the sterile type and lead to entire sterility of its pollen. A similar study of the formation of female gamete was not undertaken. But the failure of all attempts to fertilise the female gamete of the sterile plant with the male gamete of the fertile type indicates that irregularities similar to that prevailing at the time of the formation of the male gamete are probably responsible for the sterility of the female gamete as well.

The onset of abnormalities during meiosis does not become apparent until late prophase and subsequent stages. During the resting stage and sub-stages upto late prophase it was not possible to detect any difference between the nucleus of the fertile and sterile type. At diakinesis when the conjugation of homologues takes place and bivalents are formed the abnormalities in pairing first become apparent. Instead of the normal thirteen bivalents, monovalents, bivalents and multivalents are formed in the same nucleus. The separation of these at anaphase is further attended by more irregularities.

The several stages of meiotic division during gametogenesis of the male in the sterile plant are described below and the deviations from the normal or fertile type, wherever they occur, are pointed out.

(a) *Resting nucleus* :—In the resting nucleus of the pollen mother cells of the sterile plant the chromatin material aggregates at certain places (Plate II, Figs. 8 and 10) and two nucleolii are often present, while in the fertile, the faint chromatin net-work occupies the entire space within the nucleus and a single nucleolus is present.

(b) *Prophase* :—This begins with the resolving of the aggregated masses of chromatin material into a slender and long coiled mass of thread showing the beaded string-like appearance characteristic of the leptotene stage. The tangled mass of the thread is well spread and occupies the entire space within the nucleus (Plate I, Fig. 2). Further stages become obscured upto the formation of the

synizetic knot (Plate I, Fig. 3) when the entire tangled mass of chromatin thread contracts to one side of the nucleus with a loop or two of the thread projecting into the empty space of the nucleus. The tightly coiled knot uncoils itself and the pachytene or boquet stage in which the chromatin thread is thrown into a number of loops (Plate I, Fig. 7) becomes evident. The chromatin thread at the pachytene stage appears to be stouter indicating that longitudinal contraction has taken place. At a later stage with the onset of diakinesis, the thread appears to break up into a varying number of bits exceeding twenty six. At diakinesis the chromosomes which have undergone the maximum longitudinal contraction are seen to conjugate and remain evenly distributed within the nuclear membrane. In respect of conjugation the chromosomes at diakinesis do not always pair in two's. Some remain as monovalents without a partner to pair with, some conjugate in pairs, while trivalents and tetravalents are often observed. This is the first irregularity that is met with in the sterile type. Further, the total number of conjugated chromosomes is often observed to exceed the normal somatic number $2n=26$ for Asiatic cotton.

(c) *Metaphase* :—The formation of the nuclear spindle to all appearance is normal. The arrangement of the monovalents, bivalents, and multivalents at the equator of the spindle is in accord with the normal type. The type of attachment and the number of chiasmata could not be determined for want of appropriate material. At the first division of meiosis a single nuclear spindle appears and during the second division the number of spindles may vary from two to four or five (Plate IV, Fig. 20). The formation of multiple spindles results in the production of more than four microspores in the pollen mother cells. When only two spindles are formed they are of equal size and the resulting tetrad is of uniform size. When more than two spindles are formed they do not only vary in size, orientation, but also in the number of spindle fibres formed. Some of the smaller spindles have only two or three chromosomes attached. Due to the separation of chromosomes orientated on such abnormal spindles only microspores of unusually smaller size with fewer number of chromosomes are formed. (Plate V, Figs. 27, 28 and 29). In some pollen mother cells what appears to be secondary pairing becomes evident. The secondary pairing of chromosomes at the first metaphase has been observed in cotton by Weber.¹⁹ An instance of abnormal secondary pairing during second metaphase seems to have taken place as shown in Plate I, Fig. 6 and Plate III, Fig. 16.

At the time of metaphase of the first and second divisions some

pairs of chromosomes fail to form any attachment to the spindle fibre and are found scattered in the cytoplasm surrounding the nuclear spindles (Plate III, & Fig. 19). When the nuclear membrane of the daughter nuclei are formed these chromosomes become excluded. This loss in the chromosomes results in the formation of gametes having less than the normal number of chromosomes.

(d) *Anaphase* :—The disjunction of paired chromosomes during normal division takes place in a regular manner. The chromosomes withdraw to opposite poles more or less together in a group and very seldom a chromosome or two lags behind other members of the group. In the pollen mother cells of the sterile types, however, lagging seems to be of very frequent occurrence. Of all types of abnormality met with, lagging is the most frequent (Plate III, Fig. 17) and accounts for the formation of a large number of unbalanced gametes. In consequence of lagging and non-disjunction unequal distribution of chromosomes takes place. Lagging and non-disjunction take place during both the first and the second divisions of meiosis. The number of chromosomes in the resulting gametes may thus be either more or less than the normal haploid number which in the case of this Indian cotton is thirteen.

(e) *Telophase* :—The chromosomes after anaphasic separation withdraw to opposite poles and gradually lose their individualistic character; and with the formation of the nuclear membrane, disappearance of the spindle fibre, and the reappearance of nucleolus the characteristic appearance of the resting nucleus is again reinstated.

(f) *Size of chromosomes* :—In respect of the size of chromosomes of the pollen mother cells in cotton, it has been previously established, by different workers, that, of the haploid compliments of chromosome in the Asiatic cottons, twelve are of uniform size and one is larger, while in the diploid compliments twenty-four are of equal size and two are large. A careful study of the chromosome compliments of the sterile shows that there is greater variation in the size of the chromosomes (Plate I, Fig. 5 and Plate II, Fig. 9). While in normal cotton there are only two types of chromosomes in respect of size, in the sterile, there are always more than two types, and, at times, there appears to be a graded variation from the small to the large chromosomes.

(g) *Abnormalities of other kinds* :—Besides the types of irregularities mentioned above which are of frequent occurrence some other occasional types of oddities have been observed. In one case, a distorted spindle of unusual shape with chromosomes irregularly attached and distributed all along the fibres was noticed (Plate IV,

Fig. 21). Sometimes in a nucleus just beginning to enter into phases of nuclear division the chromatin material was found to be dis-integrated and diffused throughout the nucleus (Plate II, Fig. 12). While these types of unusual abnormalities may only result in the sterility of the gametes formed from them they cannot be considered to be the main cause of sterility.

V. *Discussion.*

The 1027 A.L.F. variety of cotton is a pure strain highly inbred for a large number of generations. It is highly fertile and profusely flowering throughout the season of its growth and produces large numbers of bolls. Six or seven sterile plants appeared in a crop that was raised from pure seed on the Government Farm at Surat, in the year 1932. Apparently these must have come from a single boll produced on a single plant. Otherwise if more plants had produced bolls whose seeds gave rise to sterile progeny there would have been more than six or seven sterile plants. In subsequent years observation was made on the Government Farm at Surat, and in an adjoining cultivator's field and it was found that among many thousands of plants that were fertile only a single plant happened to be sterile and produced no bolls. The origin of such a completely sterile plant must supposedly be due to mutation of a retrogressive kind. Such a type of plant must die of necessity since it cannot perpetuate its type by seed. The type of mutation resulting in complete sterility is not detrimental in effect when it occurs in a pure strain in the order of a single plant among many thousands. But if the same be the case when a pure type mutates towards a type which is either male or female sterile, the consequences may be the contamination of a pure strain with consequent loss in yield. It is easy to detect female sterility and rogue out such plants but if varying degrees of male sterility be present in pure strains as they do in apple, pear, plum, and other fruit crops they may remain undetected unless a systematic investigation is done. However, the incidence of sterility in cotton has never been so severe as to warrant such an action.

Hutchinson and Gadkari obtained two types of sterile plants from the "Million Dollar" cotton which were named 'Rogue A' and 'Rogue B.' When they attempted to propagate 'Rogue A' and 'Rogue B' by grafting, they found that the graft produced a straggling plant which produced monopodia and finally died. The 'Rogue A' and 'Rogue B' differed in one respect. 'Rogue A' had large flowers and was sterile. Otherwise it was similar to the normal "Million Dollar" in all respect. 'Rogue B' was identical with the

"Million Dollar" for all morphological characters and the only difference that could be seen was in regard to sterility. Grafted plants of 'Rogue A' and 'Rogue B' failed to survive.

In order to propagate the sterile 1027 A.L.F. cotton, both, layering and grafting were done. In both the operations the resulting plants were identical in habit and behaviour to the mother plants. The grafted plant is profusely flowering and fails to set bolls on selfing. A single boll by open pollination with a few seeds was obtained from a grafted plant; from these seeds a single progeny which is different in regard to many of the morphological characters and highly fertile has been obtained. A description of this plant will form the subject matter of another paper. What is of interest here is that grafting seems to have induced a change back to fertility, but with this difference namely change in morphological characters as well. The type of complete sterility which has appeared in 1027 A.L.F. cotton is different from that observed by Hutchinson and Gadkari in "Million Dollar" variety in that grafting has had an entirely opposite effect in these two types. 1027 A.L.F. survives and appears to be influenced in the direction of fertility due to the setting of an occasional boll but the steriles of the "Million Dollar" have died out when grafted plants were produced.

VI. Summary.

(1) A case of complete sterility in a *herbaceum* cotton and the causes leading thereto are discussed.

(2) The causes of sterility are ascribed to (a) chromosomal aberration, (b) formation of abortive pollen, and (c) sterility factor affecting the gametes which to all appearances are normal.

(3) During nuclear division preceding gamete formation the most frequent irregularity observed is that of lagging and displacement of chromosomes from the nuclear spindle. Formation of four to five spindles in a single pollen mother cell, production of microspores of abnormal sizes and exceeding the normal four from one pollen mother cell, and formation of gametes having chromosomes either in excess or less than the normal haploid complement due to irregular distribution and non-disjunction during meiosis are observed to be the contributory causes of entire sterility of the pollen of the sterile plant.

(4) Failure to effect any fertilization between the male and female gametes of the sterile with the male and female gametes of the fertile type has clearly established the complete male and female sterility of the sterile 1027 A.L.F. cotton.

(5) The sudden appearance of a few entirely sterile plants and their sporadic appearance now and again which to all outward appearances are diploid in character, is ascribed to a retrogressive mutation of the normal to the sterile type.

(6) The difference on grafting between the sterile of 1027 A.L.F. cotton and the sterile from "Million Dollar" cotton is discussed.

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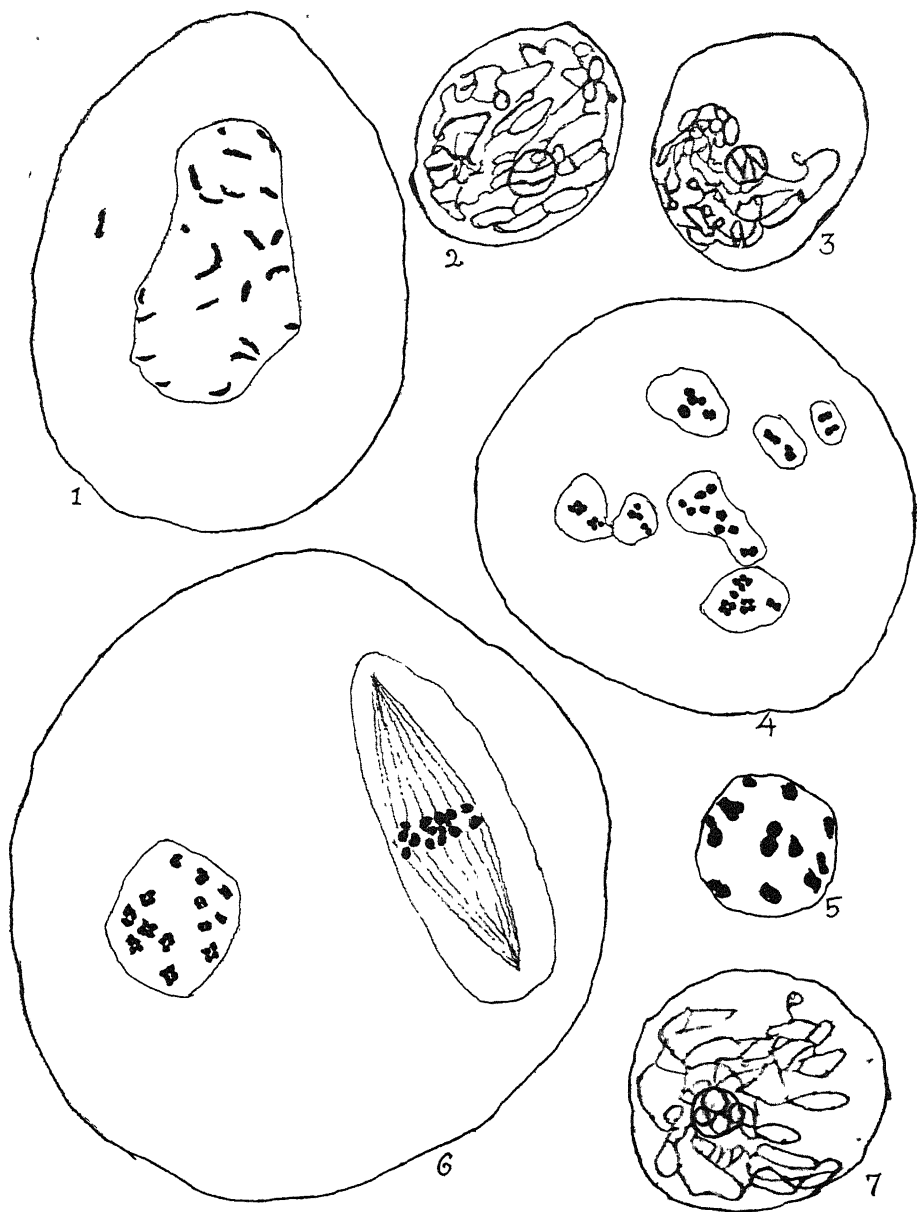
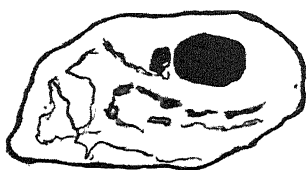
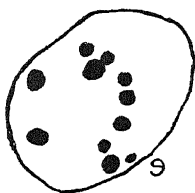


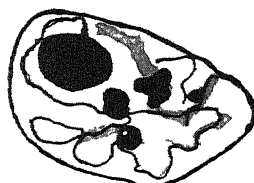
PLATE I



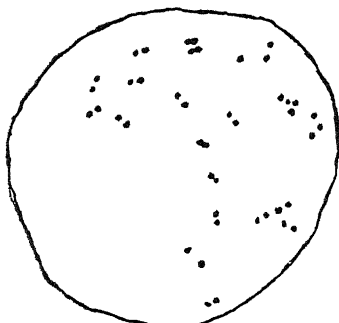
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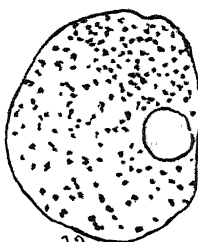
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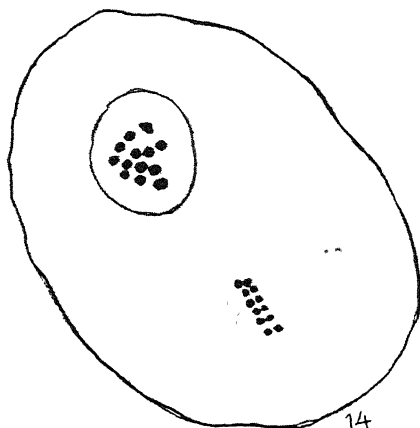
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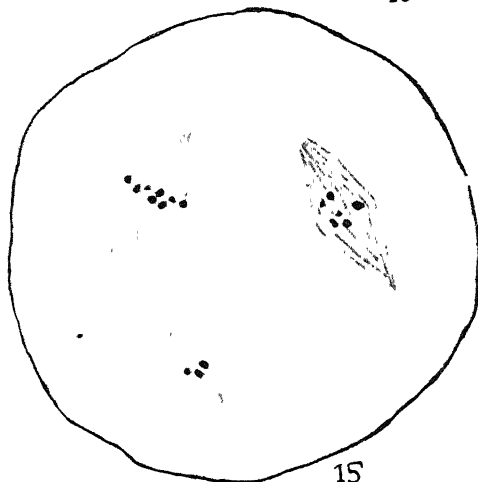
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Items 1 to 8, 11, 13 and 15 to 17 are references to papers presented at the International Conference on Flower and Fruit Sterility, held at New York on August 12th to 14th, 1926, and published by the Horticultural Society of New York in their Memoirs, as Volume 3 of 1927.

VIII. *Explanation of plates.*

PLATE I.

- FIG. 1. Chromosomes of varying shape and size distributed inside the nucleus of a pollen mother cell of the sterile plant. One chromosome is seen in the outer cytoplasm.
- FIG. 2. Leptotene stage showing the involved coiling of the chromatin thread uniformly spread out within the nucleus. A nucleolus is present.
- FIG. 3. Synizetic knot of the chromatin thread revealing the contraction of the coiled mass to one side of the nucleus.
- FIG. 4. Macro and micro nuclei present in pollen mother cell with different numbers of chromosomes. The nuclei are irregularly shaped.
- FIG. 5. Diakinesis stage. Chromosomes are grouped into bivalents and trivalents. Some have remained unpaired.
- FIG. 6. A pollen mother cell showing second metaphase of the meiotic division. One of the spindles is seen in profile and the other gives the polar view of a metaphase plate. In the latter there appears to be secondary pairing of the chromosomes.
- FIG. 7. The pachytene or bouquet stage during prophase.

PLATE II.

- FIGS. 8 and 10. The aggregation of chromatin material in a resting nucleus.

FIGS. 9, 11 and 13. Diakinesis stage. In Fig. 9 the difference in size of chromosomes is distinctly noticed. In Figs. 11 and 13 instead of the normal 13 bivalents as many as 21 bivalents and 2 univalents and 19 bivalents respectively are seen.

FIG. 12. Disorganisation of chromatin material in a nucleus about to start division.

FIG. 14. Second metaphase of the normal type seen in a pollen mother cell of the sterile plant. Thirteen the normal gametic number of chromosomes are present.

FIG. 15. Three spindles differing in their size and number of chromosomes attached to the spindle fibres in a pollen mother cell.

PLATE III.

FIG. 16. Second metaphase in a pollen mother cell. The secondary pairing of chromosomes as in Plate I, Fig. 6 is again observed.

FIG. 17. Second metaphase of a pollen mother cell showing parallel spindles with their long axis orientated in the same plane. Both show late anaphase and in one there is much lagging of chromosomes observed.

FIG. 18. Variation in number, size and pairing of the chromosomes with a few fragments of chromatin thread seen in a pollen mother cell.

FIG. 19. A pollen mother cell showing three spindles of varying sizes. Some of the chromosomes have been displaced from the spindles.

PLATE IV.

FIG. 20. A pollen mother cell showing numerous spindles of varying size. Some are seen in profile and others show the polar view of the metaphase plate.

FIG. 21. An abnormal form of spindle showing irregular attachment of the chromosomes.

FIG. 22. A pollen mother cell showing numerous spindles and a large and small vacuolate areas.

FIGS. 23 and 24. Resting nuclei with aggregation of chromatin scattered here and there.

PLATE V.

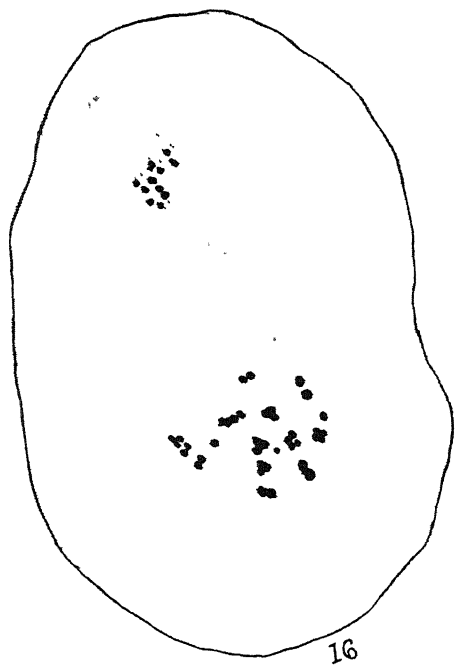
FIG. 25. Four nuclei formed after the second division in a pollen mother cell showing different chromosome numbers.

FIG. 26. Same as Plate II, Fig. 15.

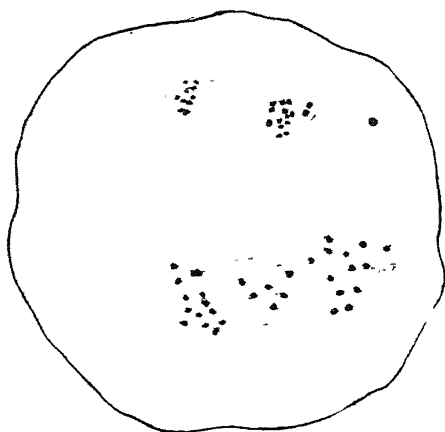
FIGS. 27, 28 and 29. Pollen mother cells showing four unequal or more than four microspores.

FIG. 30. Unusual pairing of the chromosomes.

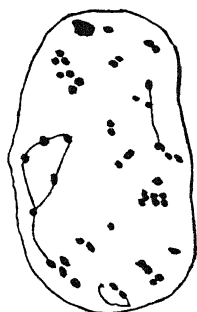
FIG. 31. Diakinesis showing abnormal pairing as in Plate II, Figs. 11 and 13.



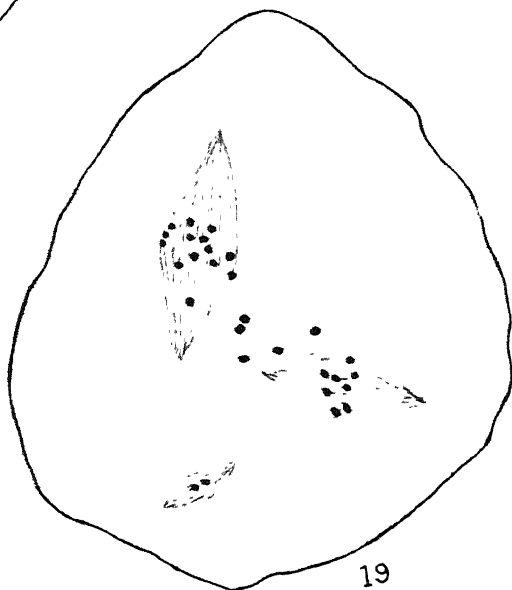
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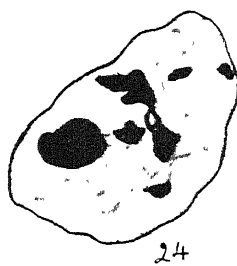
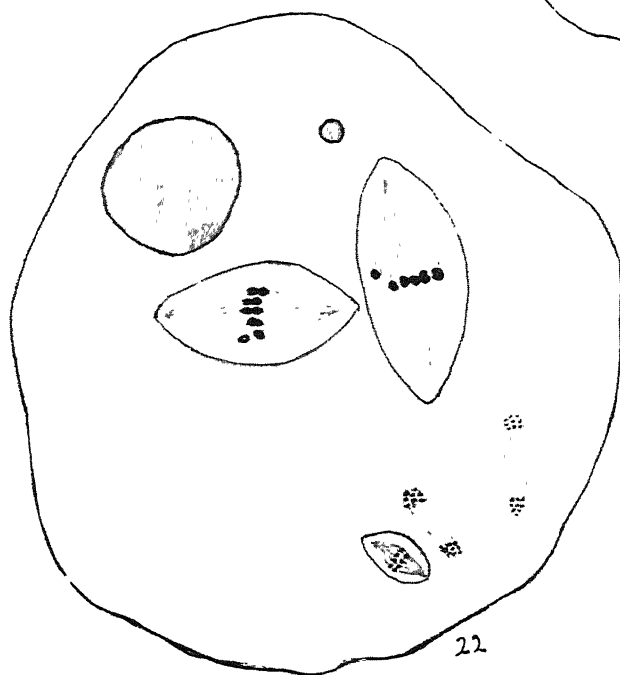
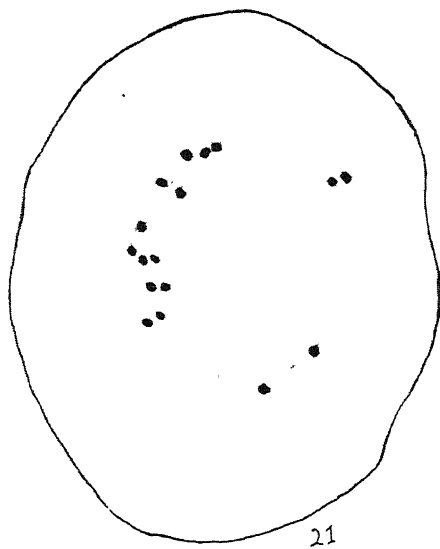
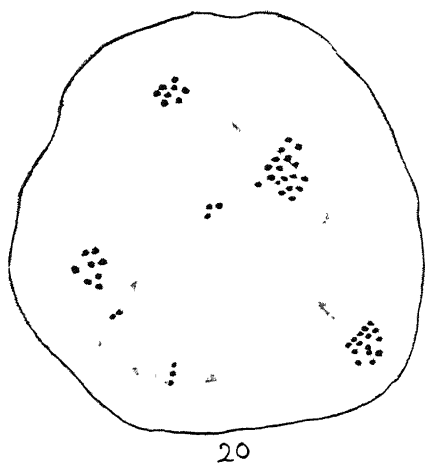
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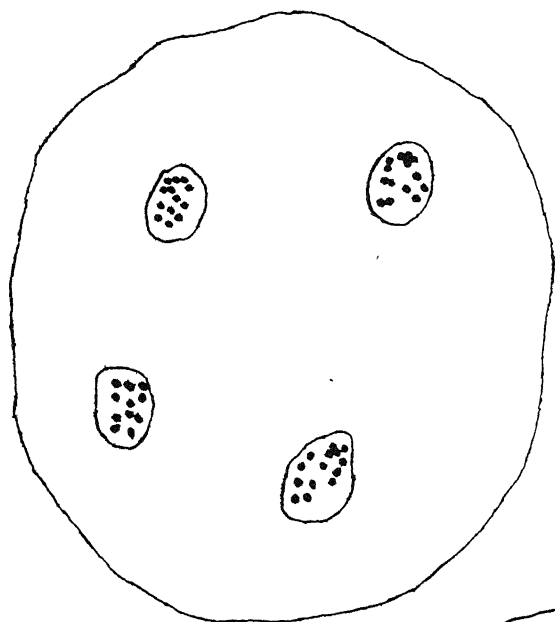


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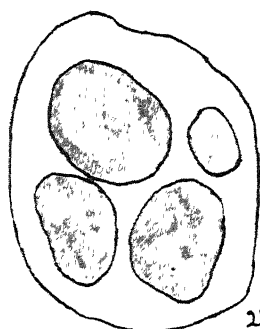


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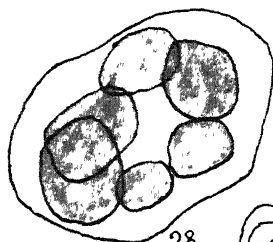




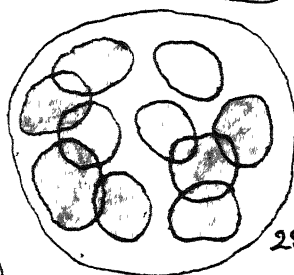
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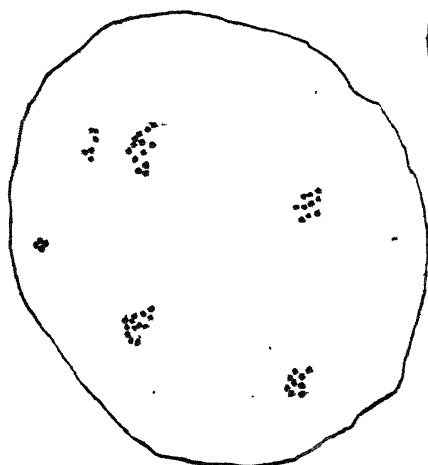
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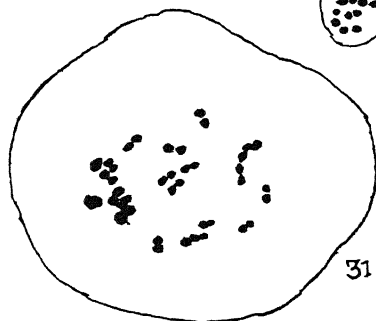
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LIFE HISTORY OF MARSILIA SP.¹ FROM POONA

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Fergusson College, Poona.

(With 73 Plate-figures.)

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INTRODUCTION.

In India much work has been done in the field of systematic Botany of the flowering plants but the Cryptogams have received very little attention at the hands of botanists and even such attention as they have received, has been from the taxonomical point of view. Very few Cryptogamic plants have been intensively studied with regard to their external and internal morphology and their detailed life-histories. The local forms of not even all Cryptogamic types which have been prescribed for study at the higher University examinations have been described in detail and students and teachers have to depend entirely on the short descriptions given in foreign text-books. It is highly desirable that local material should be investigated from the

1. For the identification of the species under consideration Baker's *Fern Allies* (1887), and Engler and Prantl's *Naturl Pflanzenfam* 1, 4, p. 403 (1902) were referred to. The description of the species does not wholly tally with that of the already described species and hence the specimens are sent to Kew Gardens, London, for identification.

point of teaching and the present paper is the outcome of observations made on one such Cryptogamic type, namely, a species of *Marsilia* collected in the neighbourhood of Poona.

Since 1870, many important papers on Cryptogams have appeared from workers like Belajeff³, Johnson⁹, Shattuck¹², Sharp¹¹ Campbell,⁵ and others. Campbell from 1888 has contributed many papers on Hydropteridae. So far as *Marsilia* is concerned he has given an account of gametophytes of *M. ægyptica* and *M. vestita*. Later on Belajeff³ gave an account of his study of gametophyte of *M. elata* and *M. vestita*; while in the same year Johnson⁹ described the development of the leaf and sporocarp of *M. quadrifolia*. It is to Shaw¹³ and Sharp¹¹, that we owe a substantial contribution regarding its spermatogenesis. Along with spermatogenesis of many other Pteridophytes Sharp¹¹ has studied spermatogenesis in *M. quadrifolia* and has given all the different stages in the four spermatogenous mitoses.

In India, however, only one paper on *Marsilia* by Pande¹⁰ has so far appeared. But his observations are mainly confined to external and internal morphology of the sporophyte and sporogenesis. In the present work the study has been extended to include gametogenesis, fertilization and embryogeny and an attempt is also made to determine the systematic position of *Marsilia* species under study.

MATERIAL AND METHODS.

Material was collected in different seasons from the river banks and marshy places near about Poona. It was killed and fixed according to methods recommended in Chamberlain's "Methods in Plant Histology" with certain modifications. According as the material was hard or soft or extremely delicate different fixatives were used. For hard material—Rhizome, petiole, sporocarps, etc.—strong chromo-acetic acid (chromic acid, 1 gm.; glacial acetic acid, 3 c.c.; water, 100 c.c.) gave satisfactory results. For soft material such as germinating mega- and micro-spores and embryos etc. a weak chromo-acetic acid (chromic acid, 1 grm.; acetic acid, 3 c.c.; water, 300 c.c.) gave the best results. This composition was found suitable after a number of trials given to other weak chromo-acetic acid solutions. Flemming's stronger and weaker solutions and also corrosive-sublimate with acetic acid were tried but not with the same success as above. The entire specimens such as sperms, embryos, funnels with sperms, etc. were preserved by the venetian-turpentine method.

For hard material safranin with Delafield's Hæmatoxylin and Orange G, and Gentian violet gave the best results. For nucleus and

chromatin material and wherever the cell divisions were followed Heidenhain's iron-alum hæmatoxylin was used.

SPOROPHYTE.

(i) *External Morphology.*

Stem :—The stem runs along the ground. It exhibits a dorsi-ventrality producing leaves on the dorsal side and roots from the ventral one. The apical growing point is covered by young leaves and trichomes. The internodes of the stem show different lengths according to the conditions (Pl. I, Fig. 1, A.C.). Branches are borne on the stem at the nodes at points slightly away from the leaf-axils.

Leaf.—Leaves are pinnately compound with four leaflets. In the bud condition they fold in a circinate manner and are covered by whitish ramenta. The petiole is slender and cylindrical. It is more or less thick at the base and tapers at the apex where it exhibits an extremely small groove between the attachments of the two inner leaflets (Pl. I, Fig. 2, c, d, g).

Root.—Roots are always adventitious. They arise at the nodes on the ventral side of the stem. They are in groups of twos or threes on either side of the median ventral line (Pl. I, Fig. 1, b).

Sporocarps.—With the advent of drier conditions the sporocarps make their appearance. Two or three sporocarps arise at each node in acropetal succession. Each sporocarp is a small pod-like structure raised on a short and slender cylindrical stock. The point of attachment is the end of the dorsal suture of the capsule and can be recognized by its proximity to the two spines which are placed one over the other (Pl. I, Fig. 1, f and h, 1, 2, 3 and 4).

The capsule is oval in form and appears like a biconvex lens. In the young condition it is green in colour and is covered with white ramentitious hairs. But as it grows the hairs are shed and the green colour is changed into brown and ultimately black. The capsule consists of two valves with five to seven sori in each (Pl. III, Fig. 17). They are united by their two edges which are recognized as the dorsal and ventral sutures. The dorsal suture is comparatively shorter. In the ripe sporocarp, the outside covering becomes hard and coriaceous.

(ii) *Internal Morphology.*

Stem :—The growing-apex in Marsilia is beset with the young leaf primordia, with the initials of the sporocarps and of the adventitious roots. It is slightly curved and is thickly covered with ramenta. It consists of a single tetrahedral cell. Out of its three internal sides two are dorsal and one ventral (Pl. II, Fig. 6, a). Segments are cut

off from these three sides in regular order, so that two rows of cells are placed on the dorsal side and one on the ventral. A few cells after the sixth or seventh segment from the apical growing point are differentiated, and according to their position, become the initial cells of the roots or of the leaves. Those on the dorsal side form the leaf initials whereas those on the ventral side form the root initials. The segments cut off on the dorsal side from the growing point further divide periclinally into two unequal cells, the larger one being directed towards the outside while the smaller towards the centre. These periclinal divisions of segments generally begin from the fourth segment, whereas the first leaf initial is seen to have been differentiated from the sixth dorsal segment (b and c). Each leaf initial in longitudinal section is two-sided (Pl. II, Fig. 9, a) along which the successive segments are cut off and thus 15 to 17 segments are formed in two rows (Pl. II, Fig. 10.) The further growth of the outer and inner segments is unequal and the rudimentary leaf assumes a curved form. At this stage the growing point slackens its activity and rapid growth takes place along the margins leading to the formation of a small fan-like structure which develops into two leaflets (Pl. III, Fig. 11). Later on two more similar structures are produced and the whole structure results in the formation of four leaflets which are placed in pairs one within the other (Pl. III, Fig. 12). This development is similar to one described by Johnson.⁹

The transverse section of the adult stem shows a distinct solenostele that is amphiplobic siphonostele. Pith is always present. Surrounding the pith there is an internal endodermal ring outside which is a thin-walled pericycle forming a single layer. Then comes the region of phloem which consists of sieve-tubes and phloem parenchyma by its side (P. II, Figs. 7 and 8).

The transverse section of the petiole shows the central vascular system surrounded completely by the endodermis. The endodermal ring is not circular as in the stem but is flattened towards one side and tends to be semi-circular. The endodermal cells have their peculiar structure. The pericycle is one-layered and below it is situated the thin-walled phloem. Xylem occurs in four groups two of which are strongly developed and form two arms of a small x. The remaining two groups consist of a few cells each arranged in a row and abutting on the pericycle on its inner side (Pl. III, Figs. 13A and 13B). The internal structure of a pinna shows that the cells of the upper and the lower epidermis are papillate possibly to help the absorption of sun-rays. Between the two epidermal layers there is a mesophyll in which lie small and large vascular bundles. Stomata

are situated on both sides of the leaf but they are much more numerous on the upper epidermis (Pl. III, Fig. 14).

Root :—The adventitious roots arise from the ventral side of the stem. Each root develops from a large prismatic cell situated a little below the growing point of the stem (Pl. II, Fig. 4, b and c). The growing point consists of a single cell having three sides and the fourth apical dome that is tetrahedral. During growth, segments are cut off along planes parallel to the three sides. This takes place in a regular order. The segments cut off from its dome-like apex form the root-cap. These observations are quite different from those of Goebel⁸ according to whom the root-cap is six-layered while in the present specimen it is nine- to ten-layered. Such a condition of the root-cap is observable even in the young root still enclosed within the sheath of the epidermis of the stem (Pl. II, Figs. 2, 3.)

The transverse section of the root exhibits a clear diarch stele (Pl. II, Fig. 5.)

The secondary roots also have the same structure as the adventitious roots except that their origin is distinctly endogenous and in this case they are derived from the pericycle opposite to the proto-xylems.

Sporocarp :—The sporocarp is a bivalved capsule and has a thick hard wall. Each valve is a hollow structure, oval in form. There runs a large mid-vein along its dorsal edge and from this 7 to 9 side-veins are given out running along the inner side of the valve. Each side-vein afterwards divides in a fork-like manner into two veinlets which do not anastomose till they reach the ventral edge of the valve (Pl. III., Fig. 16, a & b). The cavity of the valve is filled with 5 to 7 sori (Pl. III, Fig. 17), the total number in each sporocarp being 10 to 14. The wall of the sporocarp consists of a thick epidermis with many stomata. Below the epidermis, two rows of palisade-like cells are arranged at right angles to the epidermis. These cells are sclerenchymatous in nature. Inside this there is a many-layered parenchymatous tissue through which the above mentioned veins pass (Pl. III., Fig. 15).

Each sorus is placed transversely inside the sporocarp between two veins and is attached to it by its median longitudinal line. It consists of a cushion-like structure—the placenta—from the base of which a thin membranous covering arises which is the indusium. The placenta has the form of a vertical pyramidal ridge (Pl. III, Fig. 18 a). The bag-like covering known as the indusium, completely encircles the sporangia produced from the placenta. From the upper median ridge of the placenta are produced the megasporangia while from its sides microsporangia arise in basipetal succession. The megas-

porangia are the first to appear while the microsporangia are developed a little later (Pl. IV, Fig. 19 b). Each megasporangium contains only one megaspore while each microsporangium normally produces 64 microspores. There are generally four to six megasporangia and 30 to 35 microsporangia produced in each sorus (Pl. IV, Fig. 21).

Sections of young and old sporocarps (Pl. IV, Figs. 19 a and 20) show a well developed thin-walled parenchymatous tissue. This parenchymatous tissue is not uniform all over. It is thinner on the two sides while it is much more developed in a triangular space just near the peripheral ridge of the capsule. This ultimately is converted into a mucilaginous cord. The sori get loose from the wall of the sporocarp and become attached to this cord which by the imbibition of water swells enormously and comes out, carrying with it the sori attached on either side (Pl. IV, Fig. 22).

(iii) *Sporogenesis* :

A superficial cell from the placenta develops into a sporangium and it is the position of this cell which determines whether it is to be a micro- or a mega-sporangium. If it happens to be a cell on the ridge of the placenta, it develops into a megasporangium but if on its sides, it forms a microsporangium. The development of mega- or micro-sporangium from such a cell is almost the same till the formation of spore-mother-cells and subsequent tetrads. The difference lies only in the further development of the tetrads. In the microsporangium the tetrads produce numerous micro-spores while in the megasporangium only one megaspore becomes functional.

The development of the micro- and mega-sporangia upto the formation of spore mother-cells is on the same lines as in general ferns and needs no detailed description. However the figures (Pl. V, Figs. 23-30) would illustrate the same.

Reduction Division :—Meiosis has been very carefully followed, especially with a view to finding out the exact number of chromosomes in the species. The chromosome number appears to be sixteen in the haploid condition but it is yet to be definitely determined. During these observations an interesting fact was noticed regarding the planes of divisions. Generally the two spindles in the second division of the meiotic-mitosis are at right angles to each other but cases are not wanting where these were found to be parallel. The different stages in the reduction division are given in Plate V, Fig. 31, A to G.

Microsporogenesis :—A microspore is rounded in form with a tetrad mark and is .06 mm. in diameter. It is bounded by three coatings : endosporium, exosporium and episporium. The walls of the spore mother cells disintegrate and spores lie loose in the sporangium.

Megasporogenesis :—In the development of the megasporangium one cell in most of the tetrads grows bigger than the rest (Pl. VI, Fig. 33, A to D). The growth in these big cells does not keep the same pace and a condition is soon reached when a few enlarged cells from the tetrads are seen floating in the megasporangium. Ultimately, however, only one of these continues to grow at the cost of others and forms a functional megaspore. At this stage the nuclei and cytoplasm of the disorganized cells surround this large cell, the nuclei almost abutting upon the wall of the developing spore. It is not unusual to find the remaining three cells of the tetrad attached to this preferred cell, even in its later developmental stages (Pl. VI, Fig. 34). These cells also ultimately disorganize and the megaspore forms its wall. In this way only one megaspore is produced within the megasporangium (Pl. VIII, Fig. 36) and is so placed within it that its angular apex is directed towards the base of the sporangium, while its blunt base points towards its apex. During this development of the megaspore a large amount of food material, such as starch grains and oil globules, is formed inside the megaspore. At the apical part of the spore the nucleus is situated, surrounded by a little cytoplasm. This portion slightly protrudes out of the apical part of the spore and appears like a small hemispherical papilla, yellowish orange in colour. The fully grown megaspore is oval in form and ivory white in colour. Its length is 0.9 mm. and breadth is 0.7 mm. and it is surrounded by three walls. The inner-most wall is thin and membranous, the middle one is hard, being made up of prismatic rods placed with their longer axes at right angles to the surface. The outermost wall is formed of a thin mucilaginous substance.

GAMETOPHYTES

The attempts to find the gametophytes in their natural habitat were made but nothing beyond injured and decomposed sporocarps was found. Hence ripe sporocarps that had been already collected before the rainy season were kept in the laboratory for the study of their development. The following observations, therefore, were all made on plants cultivated in the laboratory. Within two hours the whole cord comes out with all the sori attached to it (Pl. IV, Fig. 22). In many cases the microspores get loose from the sporangia and float within the sorus which is still surrounded by the indusium. After some six hours or so the indusium bursts open and the mega- and micro-spores which have all the time been progressing in their germination become free in water.

(i) *Development of the Male Gametophyte and Spermatogenesis* :—Microspores are yellow in colour and almost spherical in

form with a small angular point indicated by the tri-radiate mark on the outside (Pl. VII, Fig. 44a), being on an average 0.06 mm. in diameter. A microspore has a central mass of granulated protoplasm with a large number of starch grains embedded within it. In the centre there is a nucleus with a distinct nucleolus (Pl. VII, Fig. 45). Surrounding the protoplasm there is a thin membranous wall called the endosporium, outside which is a thick exosporium consisting of prismatic cells arranged in two rows, and having small spiny protuberances. Outside the exosporium is a thin layer of mucilage forming the episporium. The presence of this mucilaginous layer possibly helps the spore to absorb and retain water.

With the absorption of water the spore becomes larger, the nucleus becomes enlarged and goes towards one side of the spore and this may be looked upon as a preparation for division (Pl. VII, Figs. 45 & 46). This takes place within an hour and a half after the spores are placed in water. The nucleus soon divides and the spore is cut off into a prothallial cell which occupies its angular side and a bigger cell which occupies the rest. The second division soon follows (Pl. VII, Fig. 47 A 2), the planes of division being almost parallel to the first. The second cell thus cut off is a bit larger than the prothallial cell but smaller than the antheridial one and occupies a position between the prothallial and antheridial cell. It contains a smaller amount of cytoplasm and can be recognized during the first few stages of development only. This cell is called the basal cell by Belajeff³ and the vegetative cell by Sharp¹¹, while the remaining cell is called the primary antheridial cell by both the authors (Pl. VII, Fig. 47A). In the antheridial cell the vacuoles formed by the absorption of water go to the periphery of the spore, while the major part of cytoplasm remains at the centre. The first two divisions described are completed within one hour and a half after germination.

The primary antheridial cell then divides into two equal halves by a wall which is generally oblique to the first wall (Pl. VII, Fig. 48, 1), and thus the secondary initials of antheridia are formed (Pl. VII, Figs. 47 B and 48, 2). Between the two antheridial initials, two sterile cells are seen in transverse sections of the microspores (Pl. VII, Figs. 50 and 51). All these changes are effected within 2 to 3 hours after the germination of the spore. From each secondary antheridial initial sterile cells are cut off in an hour or so after its formation towards the circumference of the spore while one large functional cell is formed at the centre. The first sterile cell is cut off from each antheridial initial by a wall (3), which makes generally an acute angle with the wall (2). The two walls

thus formed in the two respective initials are generally parallel to each other, so that the angles that they form with wall (2) are alternate and opposite (Pl. VII, Figs. 48, 52 and 53). The two cells again divide in a plane which cuts obliquely the wall (2) of the antheridial initial and the wall (3) of the sterile cell, cutting a small sterile cell in the angle and a large functional one (Pl. VII, Fig. 53, 4). This functional cell again divides into two, so that a long and narrow sterile cell is pushed towards the wall of the spore and a considerably large protoplasmic mass remains in the centre (Pl. VII, Figs. 53 and 54,5). Thus, in each antheridium, a protoplasmic mass with a large nucleus is separated from the original wall of the spore by these sterile cells (a & b). It is this remnant of the original protoplasmic mass of the spore that contributes later on to the formation of the spermatozooids and is, on this account, called by Sharp¹¹ the initial spermatogenous tissue. The central protoplasmic mass is then divided and sub-divided by four successive divisions and 16 spermatids are formed.

The first two divisions are at right angles to each other and the four cells formed are almost in the same plane. Pl. VIII, Figs. 58 & 59 illustrate these two divisions in the transverse as well as in the longitudinal sections. The third set of divisions divides each of these cells into two, so that eight cells are formed; but in a section all these cells cannot be seen; for, the plane of division in which each cell is divided is different (Pl. VIII, Fig. 60). The eight cells thus formed divide again into two each, resulting in the formation of 16 spermatids (Pl. VIII, Fig. 61). These 16 spermatids are so placed in the antheridial cavity that in a transverse or longitudinal section of a germinated microspore only six are seen (Pl. VIII, Figs. 62 and 63).

The centrospheres with astral rays were present in all the four spermatogenetic mitoses even before the formation of the spindles. The centrosphere was seen dividing into two and the two daughter spheres were being separated from each other to occupy the two poles (Pl. IX, Fig. 64A, B, C and D). In each spermatid the centrosphere was distinctly observed occupying a point just near the nucleus (Pl. IX, Fig. 65 A), but its actual elongation could not be observed, though an irregularly formed dotted line surrounding the nucleus accompanied by the disappearance of centrosphere was observed (Pl. IX, Fig. 65 B). This would lead one to think that this dotted line results from the metamorphosis of the centrosphere. Later stages in the formation of the blepharoplast are characterized by the transformation of the dotted line-like structure into an elongated band on which distinct dots are observed. The nucleus also changes

its form by this time and becomes elongated and joins the blepharoplast (Pl. IX, Fig. 65 C). In further development the coils of the blepharoplast increase and the whole structure resembles a top with spiral grooves. Cilia are also formed by this time and are generally present on the wider coils (Pl. IX, Fig. 65). The nucleus which also assumes a coiled form is attached to the blepharoplast by its wider coils. All these changes take place within an hour or so. Sharp¹¹ has given a detailed account of the spermatogenesis in *Marsilia quadrifolia*. The account given above does not differ from it on major points. Thus it will be seen that the male gametophyte is extremely short-lived and completes its life history within 6 or 7 hours from germination. The spermatozoid is loaded with a bag at the base which is called the vesicle. By the time it comes to the mucilaginous funnel it becomes extended, so that the number of coils is increased from 7 to 15. In this condition it appears like a long cork-screw. The cilia are shed by this time while the nucleus is situated in a few large basal coils (Pl. IX, Figs. 66 A & B).

(ii) *Development of the Female Gametophyte and Oogenesis*:—

The megaspore, while still in the sorus, attains a stage in which a prothallial papilla is distinctly formed and has burst out of the sporangial coats while a large mucilaginous funnel which is longer than broad is found at the top of the prothallial protuberance (Pl. VI, Fig. 35 B). This external change in the general appearance of the megaspore is associated with a number of internal changes that take place when the spore has begun to germinate. After three and half hours the first transverse division cutting off the megaspore into a basal prothallial cell and the upper cell takes place (Pl. VIII, Fig. 38, a). The upper cell is the initial of the archegonium. During the next two hours vertical divisions in different planes take place cutting off the archegonial initial into one central and a number of surrounding cells. The surrounding cells then divide by transverse walls forming the one-layered wall of the archegonium (Pl. VIII, Fig. 39, b). While this is going on, the central cell divides by a transverse wall into a basal and a central cell. The basal cell by further divisions forms the base of the archegonium. It is at this stage that the spores are liberated from the sorus. The further development is completed after about three hours. The central cell divides by a transverse wall into a small apical cell and a large lower one (Pl. X, Fig. 40, a and b). The small cell forms the neck-canal cell and pushes its way through the neck which is formed of four rows of two cells each. The end cell in each row is a bit longer and slightly curved outwards in the mature condition. The central cell further divides into a very small ventral-canal-cell

and a large conspicuous egg or oosphere (Pl. X, Fig. 41). In the upper part of this oosphere a small crescent-shaped depression is formed which is known as the receptive spot. This stage is completed between 9 and 11 hours and the archegonium is fully formed and ready for fertilization. The spermatozooids aggregate in the funnel even before the development of the archegonium is completed (Pl. VI, Fig. 35A).

(iii) *Fertilization* :—One of the spermatozooids enters through the neck of the archegonium. The sperm rests for a while at the receptive spot (Pl. X, Fig. 42) after which it unites with the egg and the oospore is formed.

(iv) *Parthenogenesis* :—Strasburger¹⁴ has referred to the formation of the embryo parthenogenetically. With a view to finding out if such a formation of the embryo takes place, many megaspores were segregated and their development was closely studied. In all these cases, it was found that the normal female gametophyte with the archegonium was fully developed. The prothallus invariably became comparatively larger in size and a few rhizoids were seen developing from it, but in no case was there any indication of a division in the oosphere. The archegonial wall became many-layered and the central oosphere became smaller and gradually deteriorated (Pl. X, Fig. 43) and no parthenogenesis was observed to occur in any of them.

(v) *Embryogeny* :—The fertilized egg does not show any resting condition but begins to divide immediately. Within 14 hours from the germination of the spore the oospore shows divisions and hence it can be concluded that the oospore has no resting period.

The first division of the oospore is vertical, i.e., parallel to the longer axis of the archegonium (Pl. X, Fig. 67). This takes place within a period of two hours after fertilization. The next division soon follows and the wall that is formed is at right angles to the first, dividing the oospore into equal quadrants. This quadrant-formation takes place within three to four hours after fertilization (Pl. X, Fig. 68).

Thus the oospore is divided into an upper or epibasal or anterior half having two quadrants and the lower or hypobasal or posterior half having the other two quadrants. Each quadrant then divides into two unequal octants (Pl. X, Fig. 69). From the epibasal cells of the octants are produced the root and the single cotyledonary leaf, while from the hypobasal part are given out the stem and the massive foot. The stem is produced from the quadrant which is exactly opposite to the quadrant of the root, while the foot and the

leaf lie in opposite directions. Transverse and longitudinal sections of the developing embryo clearly show the way in which these different parts of the future sporophyte are developed. The foot, as said above, is a massive structure and nearly three octants are utilized for its formation while the remaining octant forms the stem. From the generally accepted view of the physiological function of the foot this is really as it should be. The foot is only functional in the young condition of the embryo and hence is highly developed. Subsequent development of the embryo shows that the root and cotyledonary leaf grow more vigorously than the stem. This can be seen in the embryo which is a few days old (Pl. X, Figs. 71, 72 and 73).

Attempts to observe further development of the sporophyte from the fertilized egg were also made in the laboratory by keeping young embryonic plants in pots as suitable material could not be obtained from its natural habitat in the neighbourhood. The cotyledonary leaf is a thin strap-shaped structure with a pointed apex ; the second and third leaves are also strap-shaped and are developed on the stem which, by now, begins gradually to elongate. The plant after two or three weeks' growth shows the fourth leaf which has a cylindrical stalk with a small round leaflet at the apex. The very few leaves which are produced after this have two leaflets. Ultimately, the normal leaf having cylindrical petiole and four leaflets,—a characteristic of *Marsilia*—is produced. Thus the juvenile condition of the leaves shows the stages described by Bower.⁴

THE IMPORTANT FEATURES OF *MARSILIA* FROM POONA

(1) This *Marsilia* is of common occurrence in the Deccan. It is aquatic or amphibious and is also found in comparatively dry places. The external morphology shows great variations regarding the thickness of the stem, length of the internode, length of the petiole, size and margin of the leaf and its length and the occurrence of the roots.

(2) Johnson⁹ has observed the formation of the leaf initial from the third or fourth segment from the growing point of the stem and Pande¹⁰ has observed it from the 10th or 11th segment. The writer observes the leaf-initial differentiating from the sixth or seventh segment.

(3) The number of periclinal divisions of the apical cell of the root is definitely more than that observed by others. Andrews¹ and Van Teighmen have observed one layered root-cap in *M. quadrifolia* and *M. drummondii* respectively. According to Goebel⁸ five or six layered root-cap is found in *M. Salvitrix* and

Pande¹⁰ observes the same in the Marsilia from Lahore. In the Marsilia under study a definitely 8 to 10 layered root-cap is observed.

(4) The Megasporogenesis as observed in Marsilia of Poona differs from that given by Campbell⁵, Bower⁴ and Pande¹⁰ and is in a way similar to that given by Goebel⁸. According to Campbell⁵ who follows Bower⁴ only one cell in one of the tetrads gets bigger while others degenerate and it is this one cell that is ultimately converted into a megaspore. Pande¹⁰ has found in Marsilia of Lahore that only a few mother-cells divide into tetrads while others disintegrate and later on these tetrads also degenerate and the protoplasmic mass and the nuclei thus formed surround a central large vacuole. Some of these nuclei are surrounded by protoplasm and definite walls are laid round each of them and these become the megaspores. The number of such megaspores formed varies between 4 and 8 but none of them is found by him to germinate. According to Goebel⁸ on the other hand, 16 tetrads are formed and one cell from every one of these tetrads gets larger and ultimately one of these enlarged cells becomes the functional megaspore.

In Marsilia from Poona 16 tetrads are formed and in a large number of these tetrads one cell gets bigger. Some of the enlarged cells even show signs of further development so that the cells in a few tetrads are observed assuming different sizes. But ultimately only one cell out of these few becomes the largest, and forms the megaspore. It is not unusual to find the three remaining cells of the tetrad attached to this preferred cell. While this change is going on in the megaspore all the different cells in the remaining tetrads disintegrate and the protoplasmic mass and the nuclei are seen to surround this developing megaspore. Thus the formation of megaspore in the Marsilia of Poona is different from that described by the above writers.

(5) The development of the female gametophyte and oogenesis are found to confirm previous accounts.

(6) Parthenogenesis could not be observed in this plant. As many as 250 observations were made in which the megaspores, kept in a segregated condition in season and out of season, did not show any formation of an embryo. The prothallus with an archegonium was actually formed in many cases but instead of the further formation of an embryo there was observed only pronounced deterioration of the female gamete.

(7) The male prothallus and the four spermatogenous mitotic

divisions were studied. The occurrence of the second sterile cell confirms the observations of Belajeff³ rather than those of Sharp.¹¹

The centrospheres were observed in all the four spermatogenous mitoses. In the spermatid the centrosome was seen near the nucleus. With the disappearance of the centrosome there is seen a crescent-shaped dotted structure near the nucleus. This confirms the suggested transformation of a centrosphere into blepharoplast as given by Sharp¹¹.

(8) The study of the embryogeny has revealed no new facts.

In conclusion I have to thank Prof. D. L. Dixit for his guidance and the keen interest he took while the work was in progress. Thanks are also due to Prof. V. V. Apte of our college for the useful suggestions made by him from time to time.

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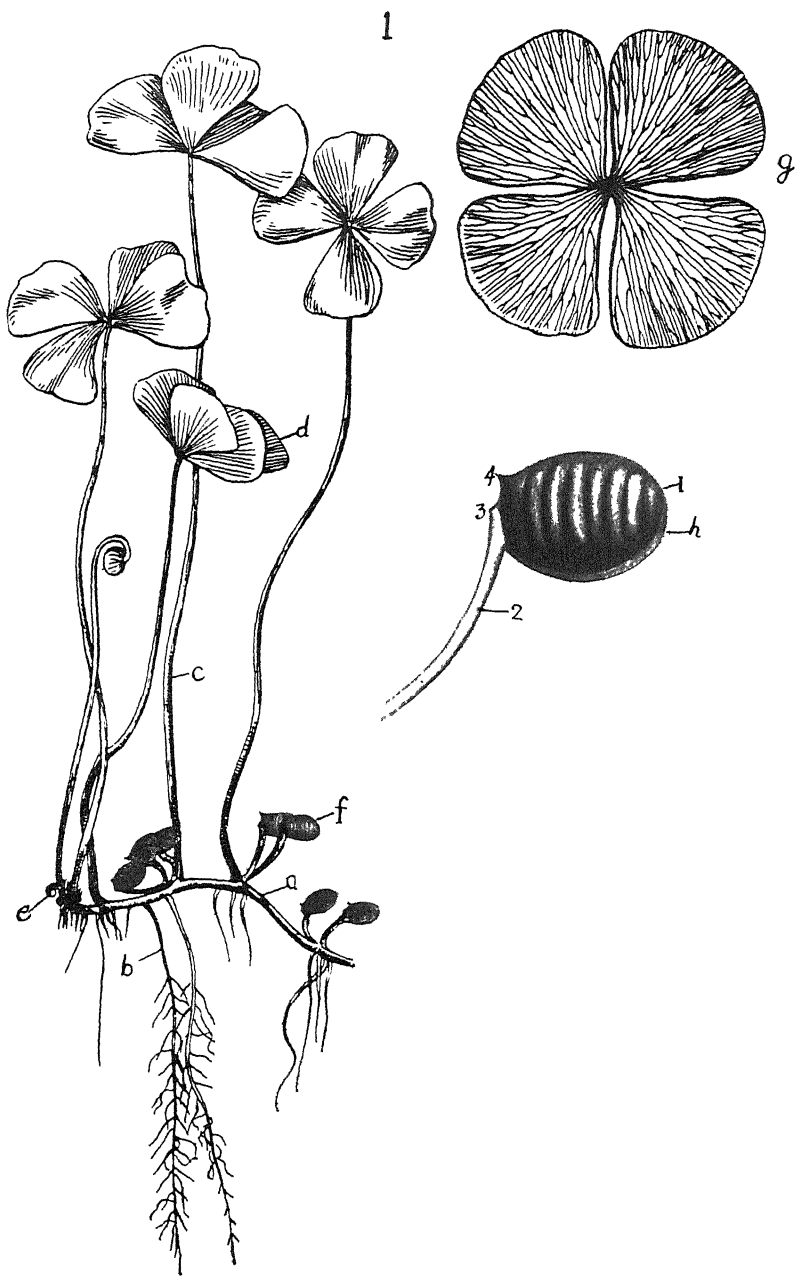


PLATE I

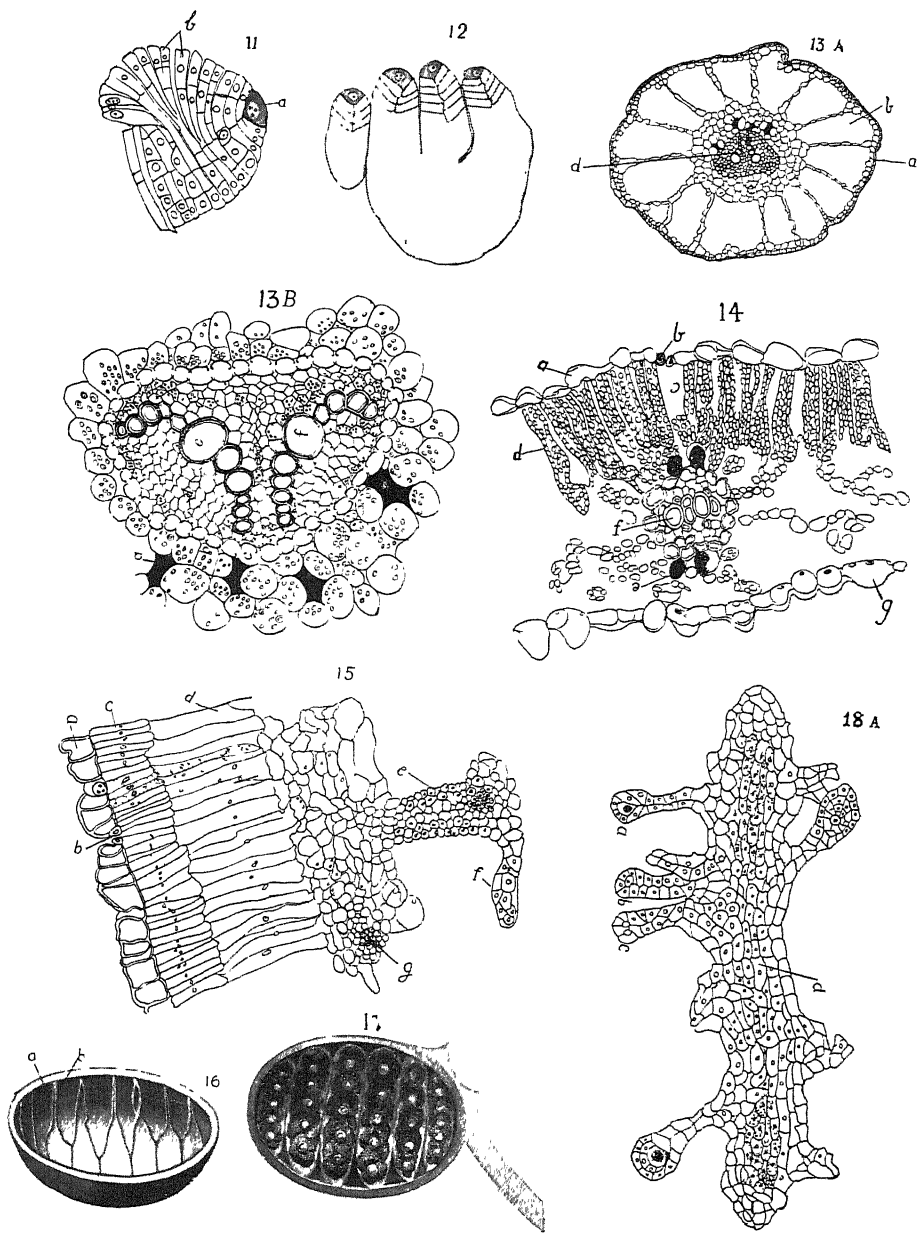


PLATE III

EXPLANATION OF PLATES

The figures are drawn with the help of an Abbe's Camera Lucida.

The initial magnification is indicated with the description of each figure.

Only Figs. Nos. 18 A and 18 B ; 23 to 28 ; 31 ; 45 ; 46 ; 48 to 58 ; 60, 62 and 63 are enlarged twice by means of pentagraph.

All the figures are reduced to half in the reproduction of the photographs except Figs. 64 A to 66 B.

PLATE I.

- Fig. 1. Diagram of a plant with different organs (natural size) a, Stem; b, Root; c, Petiole; d, Lamina; e, Growing point; f, Sporocarp with pedicel and capsule; g, Pinnately compound leaf with four leaflets showing venation; h, Sporocarp magnified; 1, Ridge; 2, Stalk; 3, Lower tooth; 4, Upper tooth.

PLATE II.

- Fig. 2. L. S. of an adventitious root just near the growing point. a, Epidermis; 1 to 5, Layers of root-cap. x 530.
- Fig. 3. L. S. of the growing point of root (somewhat older than of Fig. 2). a, Epidermis of the stem; 1 to 10, Layers of root-cap. x 530.
- Fig. 4. L. S. stem-apex showing root primordia. a, Growing point of the stem; b and c, Root primordia; d, Young leaf; e, Vascular strand. x 310.
- Fig. 5. T. S. of the root. a, Piliferous layer; b, Air space; c, Thick-walled cortex; d, Endodermis; e, Phloem; f, Xylem. x 310.
- Fig. 6. L. S. of the growing point of stem, showing leaf-primordia. a, Apical cell; b and c, Leaf initials; d, Hairs. x 530.
- Fig. 7. T. S. of the stem. a, Epidermis; b, Air-chamber; c, Thin-walled cortex; d, Thick-walled cortex; e, Endodermis with stele. x 60.
- Fig. 8. T. S. of the central stele of the stem magnified; a, Cortex; b, External endodermis; c, External phloem; d, Xylem; e, Inner phloem; f, Inner endodermis; g, Pith; h, Tannin sacs. d, e, f, and g are placed in the respective tissues. x 120.
- Fig. 9. L. S. of the leaf growing-apex. a, Apical cell; b, c, and d, Sporocarp-initials. x 530.
- Fig. 10. L. S. of a very young leaf showing 15-17 segments; a, Hairs; b, Apical cell. x 530.

PLATE III.

- Fig. 11. L. S. of a leaf somewhat older than that of Fig. 10. a, Main growing point; b, Fan-like structure forming the pinna. x 530.
- Fig. 12. L. S. of a very young leaf showing four pinnae with marginal cells which look like four apical growing points. x 310.
- Fig. 13A. T. S. of the petiole. a, Epidermis; b, Air lacuna; d, Central stele. x 60.

- Fig. 13B. T. S. of the stele of the petiole magnified. a, Tannin sacs ; b, Cortex ; c, Endodermis ; d, Phloem ; e, and f, Xylem. x 310.
- Fig. 14. T. S. of the pinna. a, Upper epidermis ; b, Stoma ; c, Air-passage ; d, Palisade tissue ; e, Tannin sacs ; f, Vascular strand ; g, Lower epidermis. x 530.
- Fig. 15. T. S. of the wall of the sporocarp. a, Epidermis ; b, Stomata ; c, and d, Sclerenchymatous wall ; e, Placenta ; f, Stalk of the microsporangium ; g, Vascular strand x 530.
- Fig. 16. Sporocarp valve showing veins with branches that run parallel (a and b). x 10.
- Fig. 17. Sporocarp valve with six sori. x 10.
- Fig. 18A. Section of a placental ridge d with microsporangia a, b and c. x 120.

PLATE IV.

- Fig. 18B. Section of Sori passing through the middle portion of the developing megasporangia. a, b, c, and d, Megasporangia. x 60.
- Fig. 19A. L. S. of a sporocarp just near the growing apex. a, Stalk ; b, sorus. x 310.
- Fig. 19B. L. S. of the same sorus as in 19A magnified. a, Placenta ; b, Initial cell of megasporangium ; c, and d, Initial cells of microsporangia. x 900.
- Fig. 20. T. S. of a young sporocarp. a, Epidermis ; b, Sub-epidermal layer ; c, Sorus ; d, Young megasporangium ; e, Very young microsporangium ; f, Vascular strand. x 310.
- Fig. 21. A sorus magnified. a, Megasporangium ; b, Microsporangium. x 60.
- Fig. 22. Sporocarp with the cord and 12 sori magnified. a, Sporocarp ; b, Cord ; c, Sorus.

PLATE V.

- Fig. 23. Placenta with sporangial initials ; a, Placenta, b, Oblique wall cutting the initial into inner and outer cells ; d, Inner cell ; e, Outer cell. x 530.
- Fig. 24. L. S. of young sporangium with apical cell. a, An apical pyramidal cell. x 530.
- Fig. 25. L. S. of young sporangium. a, Wall ; b, Tapetal layer ; c, Archesporium. x 530.
- Fig. 26. Same as Fig. 25. with archesporial cell divided into two cells. a, Wall ; b, Tapetum. x 530.
- Fig. 27. Same as Fig. 26 with four cells formed. a, Wall ; b, Tapetum. x 530.
- Fig. 28. Same as above with spore-mother cells formed. a, Spore mother cells ; b, c, and d, Layers of tapetum ; a, Wall. x 530.
- Figs. 29 & 30. L. S. of a sporangium. a, Spore-mother cell ; b, Disorganized tapetum. x 530.
- Fig. 31. Different stages of the reduction division. x 900. A, Spore-mother-cell showing synaptic phases ; B, Formation of the first large spindle ; C, Two daughter nuclei again dividing,

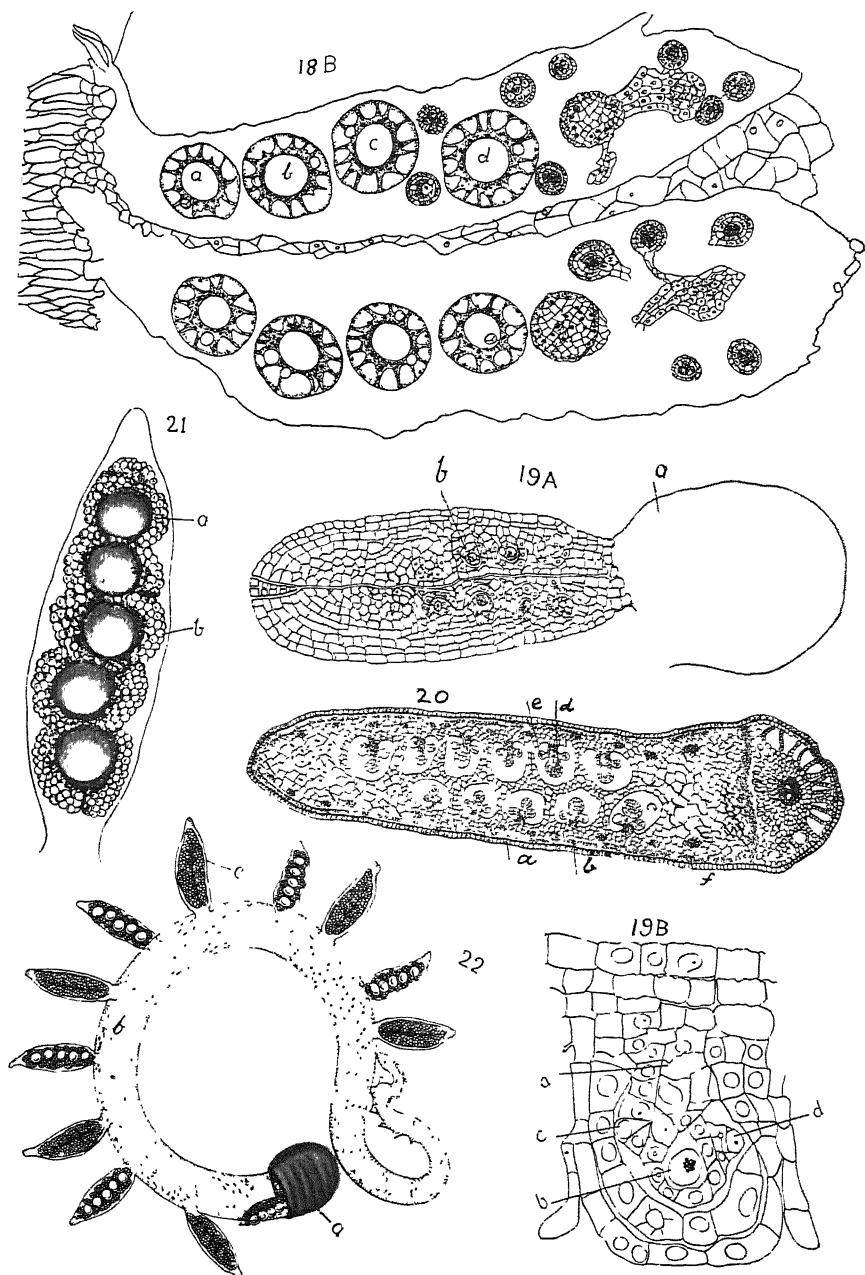
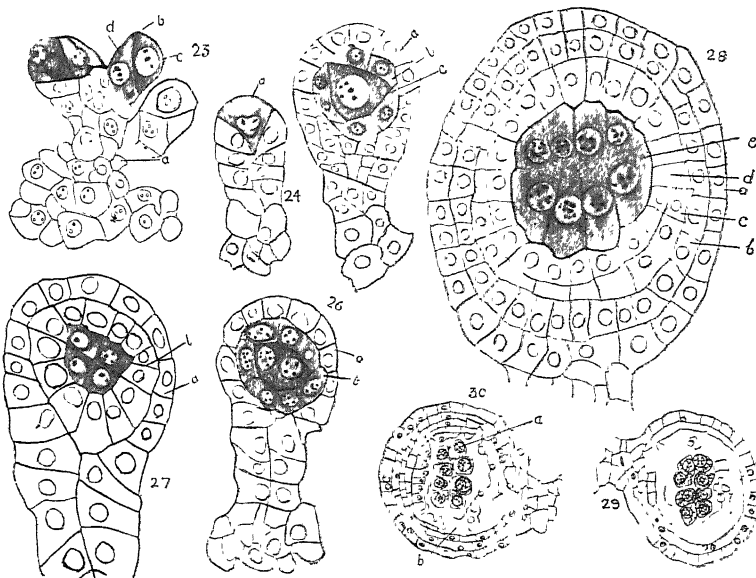


PLATE IV



31A



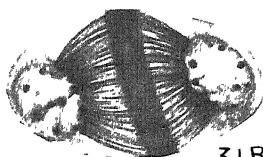
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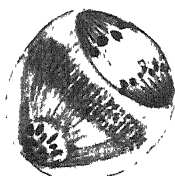
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31B



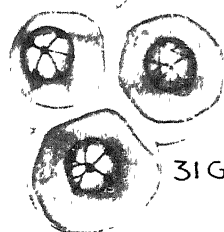
31E



31C



31G



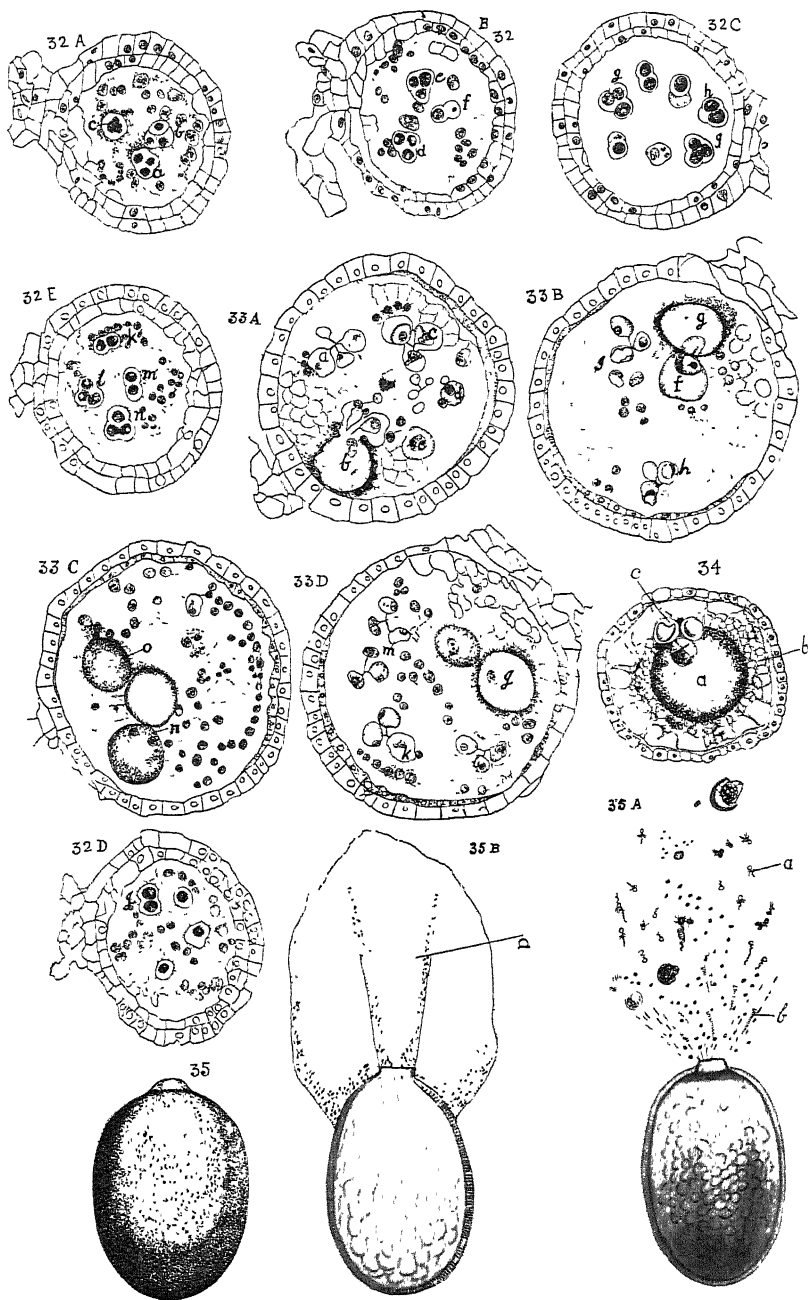


PLATE VI

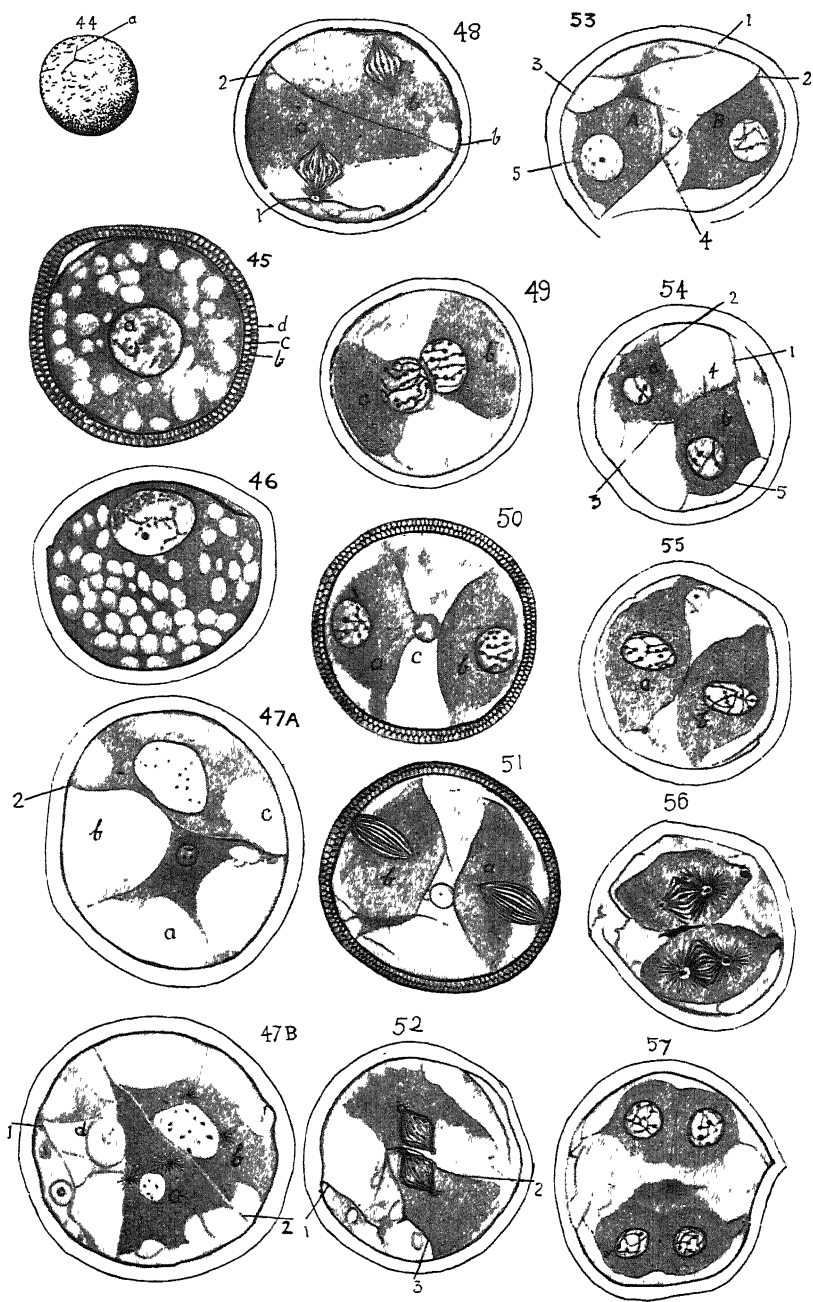


PLATE VII

one in the spindle stage and the other in the process of division ; D, Two parallel spindles ; E, Second division, with the two spindles are at right angles to one another ; F, Tetrad formation with the formation of cell-plates at the equatorial region ; G, Developing daughter-spores.

PLATE VI.

- Figs. 32A to E. Serial longitudinal sections of a single megasporangium. a, to n, Tetrads. x 530.
- Figs. 33A. to D. Serial Longitudinal sections of a single megasporangium showing one cell from many of the tetrads enlarging. x 530. a to j, Enlarged cells.
- Fig. 34. L. S. Megasporangium. a, Enlarged spore ; b, Disorganized protoplasmic mass of other spores ; c, Three remaining cells of the tetrad attached to the megaspore. x 530.
- Fig. 35. A ripe megaspore magnified. x 60.
- Fig. 35A. Megaspore with sperms at the apical portion. a, and b, Sperms. x 60.
- Fig. 35B. Megaspore with funnel. a, Funnel. x 60.

PLATE VII.

- Fig. 44. Entire spore magnified. a, Tetrad mark. x 60.
- Fig. 45. Section of ungerminated microspore. a, Nucleus and nucleolus ; b, c, and d, Walls of the megaspore. x 530.
- Fig. 46. Section of a microspore in which the enlarged nucleus has gone towards one side of the spore. x 530.
- Fig. 47A. L. S. of a micro-spore two hours after germination. a, Prothallial cell ; b, Second sterile cell ; c, Primary antheridial cell ; 1, First wall ; 2, Second wall dividing the cell into the sterile cell and the primary antheridial cell. x 760.
- Fig. 47B. L. S. of the microspore of Fig. 47A in which the primary antheridial cell has divided into two initials of antheridial by a wall 2. 1, Prothallial wall ; a, and b, Initials of antheridia ; d, Nucleus of the second sterile cell. In both the cells centrosomes are seen near the nucleus. x 760.
- Fig. 48. L. S. of a microspore three hours after germination. 1, Wall of the prothallial cell ; 2, Wall No. 2 ; a, and b, Initials of antheridia. x 530.
- Figs. 49. to 51. T. S. of microspores three hours after germination, showing the two antheridia in two halves a and b, and sterile cells in the centre.
- Fig. 52. L. S. of a microspore showing the formation of second sterile cell in each antheridium. First three walls are indicated by numerals 1 to 3. x 530.
- Figs. 53 & 54. L. S. of microspores after four hours and a half from germination. A, B, a, and b, Central spermatogenous cells. Walls are indicated by numerals 1—5. x 530.
- Fig. 55. T. S. of a microspore. a, and b Spermatogenous cells in two halves. x 530.

Figs. 56 & 57. T. S. of microspores showing the first spermatogenous mitosis. x 530.

PLATE VIII.

Fig. 58 T. S. of a microspore showing four cells in each half. x 530.

Fig. 59. L. S. of a microspore with four cells in each group. 1 to 5, Walls. x 760.

Fig. 60. T. S. of a microspore showing the third spermatogenous mitosis. x 530.

Fig. 61. A part of T. S. of a microspore showing the formation of spindles in the fourth mitosis.

Fig. 62. T. S. of a microspore six hours after germination, showing two ripe antheridia and 6 spermatids out of the 16 in each. x 530.

Fig. 63. T. S. of a microspore fixed between 6 to 7 hours from germination. a, Blepharoplast. x 530.

Fig. 36. L. S. of a megaspore in the sporangium. a, Wall of the sporangium; b, Outer wall of the megaspore; c, Prismatic rods; d, Inner wall. x 310.

Fig. 37 Enlarged protoplasmic mass at the apical portion of a megaspore with the nucleus. x 530.

Fig. 38. L. S. of a developing female prothallus with (a) the first transverse wall and (b) the second vertical wall. x 530.

Fig. 39. L. S. of a megaspore papilla in which the female prothallus is formed. a, Central cell; b, Wall of the archegonium. x 530.

PLATE IX.

Figs. 64A. to D. The fourth spermatogenous mitosis showing the centrosphere in different stages of division. x 2160.

Fig. 65A. A spermatid with the centrosome or blepharoplast. x 2160.

Fig. 65B. An irregularly shaped blepharoplast with the nucleus on one side. x 2160.

Figs. 65C. & D. Later stages in the development of a blepharoplast. x 2160.

Fig. 65E. Stage later than in Fig. 65D, in which coils and cilia are seen. x 2160.

Fig. 66A. A Spermatozoid shortly after the escape from the microspore with 6 to 7 coils and cilia and the vesicle cast off. x 2160.

Fig. 66B. A fully extended spermatozoid from the gelatinous funnel of the megaspore with 16 to 17 coils without vesicle and cilia. x 2160.

PLATE X.

Fig. 40. L. S. of a megaspore papilla in which the central cell is divided. a, The cell; b, Neck-canal cell; c, Wall. x 530.

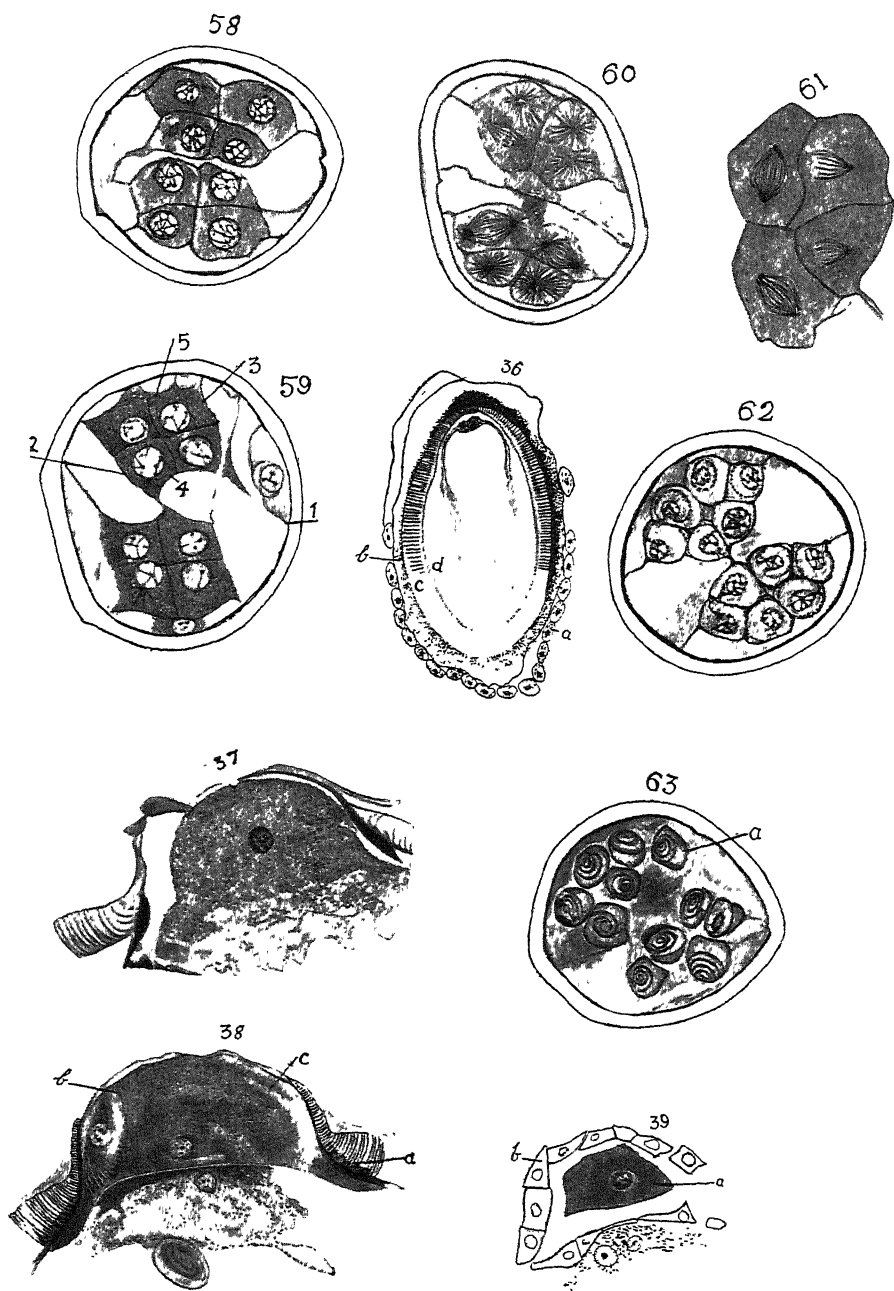
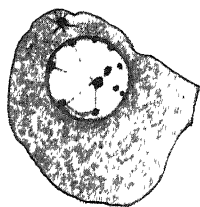
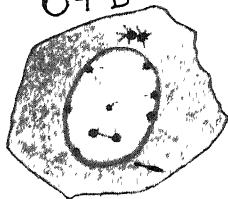


PLATE VIII

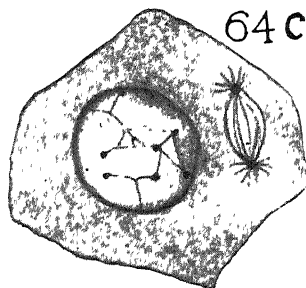
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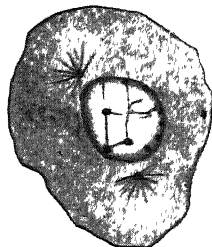
64 B



64 C



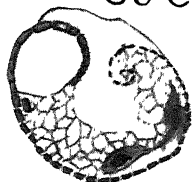
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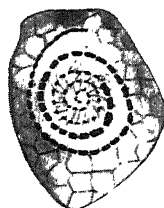
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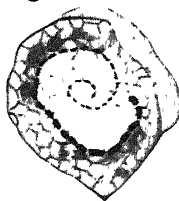
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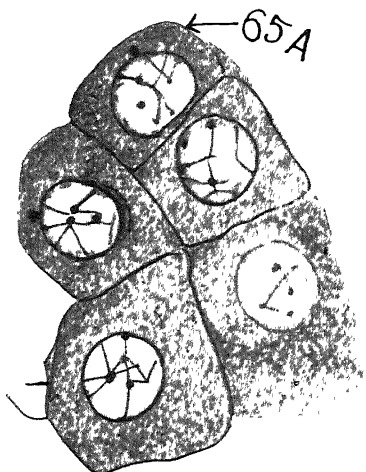
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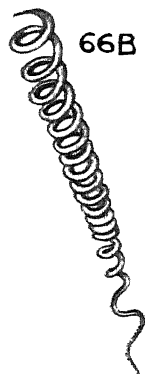
65 D



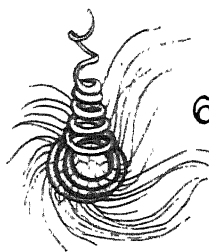
65 A



66 B



66 A



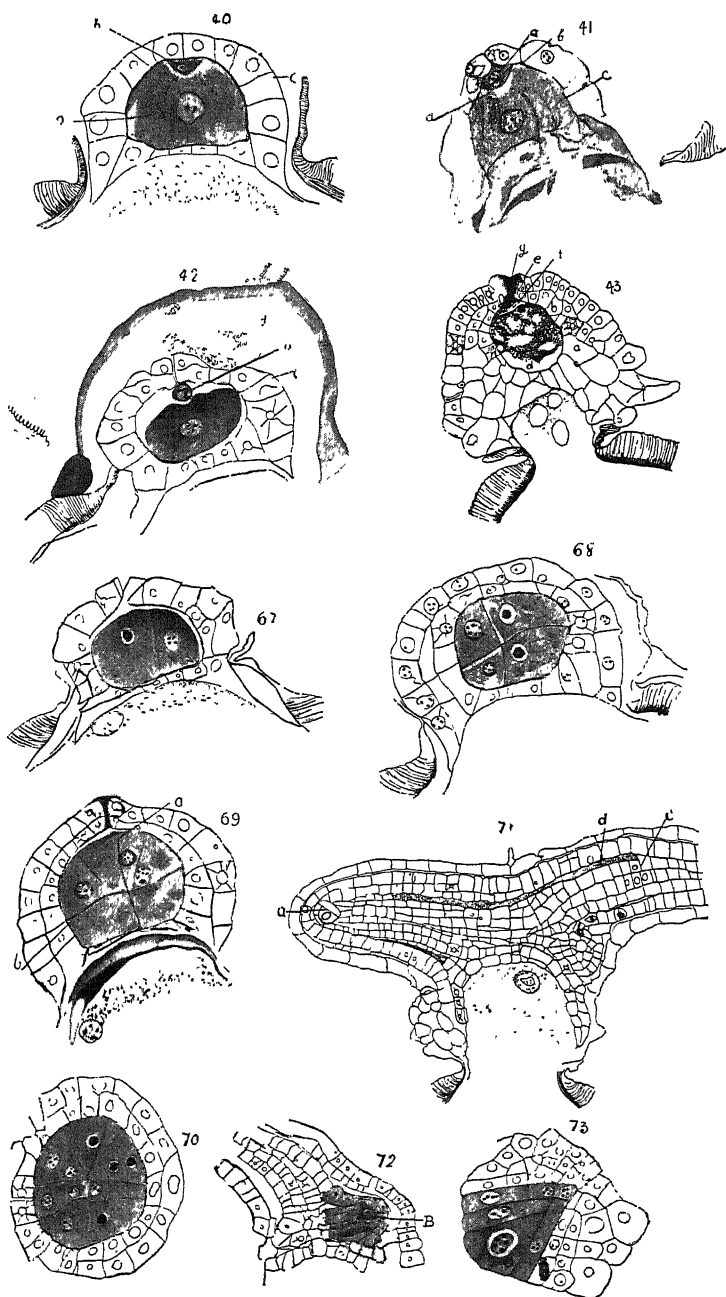


PLATE X

- Fig. 41. L. S. of a fully formed archegonium at the apex of the megaspore. a, Neck-canal cell ; b, Ventral-canal cell ; c, Egg ; d, Receptive spot. x 530.
- Fig. 42. L. S. of a fully developed archegonium before fertilization in which the neck-canal cell and ventral-canal cell are disorganized. a, Sperm on the receptive spot ; b, Egg ; c, Wall ; d, Portion of the disorganized sperms at the mouth of the archegonium. x 530.
- Fig. 43. L. S. of unfertilized prothallus and archegonium after two days showing the development of many layered archegonial wall and deteriorated female gamete. a, b, and c, Walls ; d, Egg ; e, Neck-canal cell ; f, Ventral-canal cell ; g, Neck. x 530.
- Fig. 67. L. S. of an embryo with the first vertical wall (about two hours after fertilization). x 530.
- Fig. 68. Same as above showing the quadrant stage, about 3 to 4 hours after fertilization. x 530.
- Fig. 69. Same as above with the octant stage. a, and b, Epibasal and hypobasal walls about 6 hours after fertilization. x 530.
- Fig. 70. T. S. of a young embryo after the octant stage. x 530.
- Fig 71. Median L. S. of a young embryo after 24 hours from fertilization. a, Apical cell of the root ; b, Apical cell of the stem ; c, Cotyledon ; d, Air lacuna. x 31.
- Fig. 72. L. S. of a part of an embryo showing apical cell of the root magnified. B, Apical cell. x 900.
- Fig. 73. Same as above showing the apical cell of the stem magnified. a, Apical cell. x 900.

THE MUSCULATURE AND MOVEMENT OF THE ZYGOTEROUS DRAGON FLY LARVA

(With two text figures)

By

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Introduction and historical survey.

Considerable work has already been done on the muscles of the Odonate larva by Backhoff (1910), Schmidt (1915), Wallengren (1914), and Steiner (1929). Whedon (1919) in his paper on the Morphology of the Odonate abdomen has given a detailed account of the different muscles found in the Zygopterous and Anisopterous larvae. Apart from the mere description of the muscles, no attention has yet been paid to the working of these muscles, as to which of these muscles are responsible for bringing about the peculiar bending movements of the abdomen which propel the larva forward in water. The generalized plan of muscle arrangement in Zygopterous larva is the same as in insects in general as pointed out by Snodgrass in his book "On the Morphology of the Insect abdomen." He says "The fundamental plan of muscle arrangement in Odonata is that of Pterygote insects in general, and has little to distinguish it from the muscle pattern of Orthopteroid insects." I, therefore, propose to give in this paper the results of a detailed investigation of the musculature of the Zygopterous larva which show how, keeping within the limits of the fundamental plan, nature has modified the musculature of the insect to suit the peculiar requirements of an actively moving aquatic life.

According to Snodgrass the musculature of a generalized insect consists of the following groups of muscles.

- I. External and internal longitudinal dorsal divided into median and lateral dorsals. (emdm, eldm, imdm, ildm, Fig. I).
- II. External and internal longitudinal ventrals also divided into median and lateral ventrals. (emvm, elvm, imvm, ilvm, Fig. I).

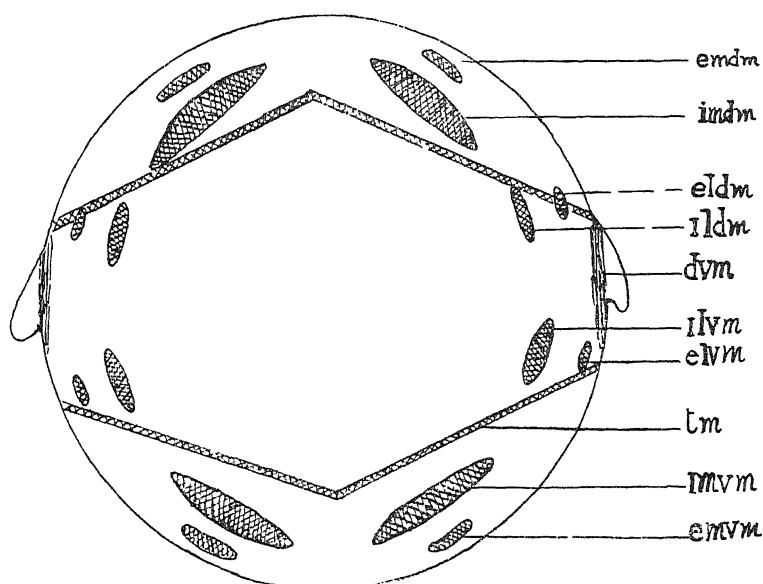


Fig. I. A plan of the musculature of a generalized insect.

III. Dorso-ventral muscles. (dvm. Fig. I).

IV. Transverse muscles. (tm. Fig. I).

Whedon's terminology for the above named muscles is different. His naming of the muscles of the Zygopterous larva is as follows :

I. Primary longitudinal dorsals and ventrals.

II. Tertiary-longitudinal dorsals and ventrals.

III. Quaternary-longitudinal dorsals and ventrals.

It is obvious from the description of the muscles that the primary longitudinal dorsals and ventrals of Whedon correspond to the internal longitudinal dorsals and ventrals respectively. The tertiary and quaternary longitudinal dorsals and ventrals correspond to the external median and external lateral longitudinal dorsals and ventrals respectively.

Material and method.

Specimens of Zygopterous larvae were obtained from ponds round about Bombay. The muscles were studied by dissection as well as from sections. The measurements of muscles given are from transverse sections from the middle region of the abdomen of an *Agrion* larva. Sections of *Agrion* larvae were kindly loaned to me by Dr. George. According to Dr. George the section used for measurements was of a fully developed larva.

Muscles of Zygopterous larva.

In the Zygopterous larva the following muscles are easily seen.

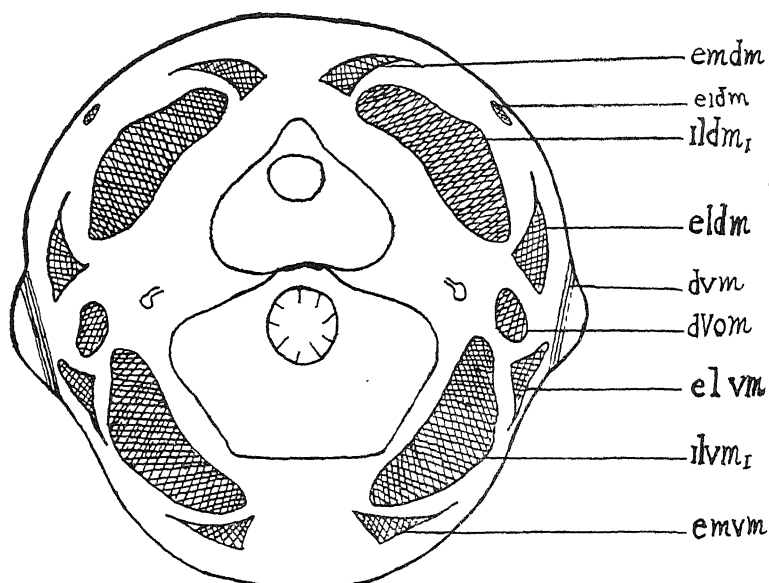


Fig. II. T. S. of Agrion-larva passing through the middle of the Abdomen.

I. Internal longitudinal dorsal muscles. ($ildm_I$, fig. II). These are two distinct blocks of muscles placed dorso-lateral to the long axis of the body. Each block is a compact group of muscle bundles, and is not divided into median and lateral bands. The muscles are intra-segmental and are of segmental length. Each block is about two-fifth the width of the tergum. The width of the tergum is 1.92 m.m. while the width of each band of muscles is .7 m.m. Both blocks together occupy four-fifth the width of the tergum.

II. Internal longitudinal ventral muscles. ($ilvm_I$, fig. II). Similar to the internal dorsals the internal ventrals are formed into two distinct blocks arranged symmetrically in a ventro-lateral position. The measurements of these muscle blocks show that these are thicker blocks of muscles than the internal dorsals, each band being .75 m.m. thick. The dorsals correspond in position to the ventrals.

III. The external dorsals. These muscles occur in two groups being differentiated into external median ($emdm$ fig. II) and external lateral ($eldm$ fig. II) dorsal muscles.

(1). External median dorsals. ($emdm$, fig. II). These are two distinct blocks, one on either side of the mid-dorsal line. Each block is .21 m.m. thick which shows that these are smaller blocks of

muscles. They are thicker towards the median line of the animal and gradually narrow towards the sides.

(2). External lateral dorsal muscles (eldm fig. II). They are situated laterally overlapping the lateral portion of the internal dorsals. These muscles are thicker medially and progressively narrow towards the sides. Both the external median and external lateral dorsals are intra-segmental and are of segmental length though Whedon is of opinion that these muscles are not of segmental length.

IV. *External ventrals*. (emvm, elvm, fig. II). These correspond to the dorsals except for their smaller size.

Besides the external dorsals and ventrals a small block of muscles is seen in the larva of which no mention has been made by Whedon. This is a small block of muscle situated midway between the external median (emdm, fig. II) and external lateral (eldm, fig. II) dorsal muscles. According to its position it can be named external intermediate dorsal muscle (eidm, fig. II) though no corresponding ventral is found. It is about half the length of the segment.

V. *Dorso-ventral muscles* (dvm, fig. II). These are essentially the tergo-sternal muscles. They pass along vertically from tergite to sternite near the pleural margin. These are comparatively thin delicate muscles, the whole band being composed of a limited number of fibres. Their origin is on the dorso-lateral line of the tergite while their insertion is on sternite near the pleural margin.

VI. *The Dorso-ventral oblique muscles*. (dvom fig. II.) These also run tergo-sternally but are obliquely placed. Their origin is on the suture fold of the tergite a little lateral to the internal dorsals while they pass obliquely downwards, their insertion being on the sternal suture of the same segment.

Discussion.

From the foregoing description of the musculature of the Zygopterous larva, it is clear as pointed out by Snodgrass that the plan is that of the generalized insects. Nevertheless the modifications undergone by these muscles are so conspicuous as to warrant special notice. The chief feature of the modification is, (1) the fusion of the internal median dorsal and internal lateral dorsal into a huge block of muscle placed dorso-laterally. (2) The fusion of the internal lateral ventral and median ventral into a correspondingly huge ventro-lateral block. Both these pairs of muscles are very conspicuous in the cross sections of the larva. These muscles, on account of their position and size, are analogically similar to the myomeres of the tail region of fishes and help the larva in its progress.

When a body is moving through water at a constant speed the body must be constantly supplied with energy. In the case of the

fish the requisite energy is supplied by the muscles. According to Dr. Gray the energy so supplied is applied in such a way as to exert a backward thrust on water which compensates the resistance exerted by the water on the body of the moving fish. So also in the case of the Zygopterous larva. The motion of the larva in water can be compared to that of an eel because in both the whole body acts as a propeller and a series of waves that are produced by the repeated bending of the body makes the fish or the larva go ahead. Suffice to say that the forward thrust of the larva can only be effected if the waves that are produced by the muscular contraction pass at a greater speed than that at which the larva is moving. These waves of muscular contraction are produced by the internal longitudinal dorsal (ildm₁, fig. II) and internal longitudinal ventral (ilvm₁, fig. II) muscles. When the muscles on one side of the body contract, its neighbours on the opposite side are fully relaxed and a complete bending of the abdomen to one side is effected. By the repeated contraction and relaxation of the muscles there is a repeated bending of the abdomen on both the sides and consequently a series of waves are produced which make the larva move forward in water.

SUMMARY

I. The musculature of the Zygopterous larva consists of the following groups of muscles.

1. Internal longitudinal dorsals (ildm, fig. II) and ventrals (ilvm, fig. II) not divided into median and lateral blocks.
2. External longitudinal dorsals and ventrals divided into external median (emdm, emvm, fig. II) and lateral (eldm, elvm, fig. II) longitudinal dorsals and ventrals.
3. Intermediate dorsal muscles. (idm, fig. II).
4. Dorso-ventral muscles. (dvm, fig. II).
5. Oblique segmental muscles. (dvom, fig. II).

II. From the musculature of the Zygopterous larva it is clear that it is that of a generalized insect. Still there are certain modifications. The chief feature of the modifications being fusion of the internal median dorsal (imdm, fig. I) and internal lateral dorsal (ildm, fig. I) into a huge block of muscles placed dorso-laterally and the fusion of the internal median ventral (imvm, fig. I) and internal lateral ventral (ilvm, fig. I) into a correspondingly huge ventro-lateral block.

III. The movement of the larva in water is like that of an eel. The forward propulsion is effected by the waves set up in water by the contraction and relaxation of the internal longitudinal dorsal

(ildm, fig. II) and internal longitudinal ventral (ilvm, fig. II) muscles which are placed somewhat laterally unlike what is obtainable in other insects.

Before concluding this paper I wish to express my gratitude to Dr. George for the loan of his slides and also for his suggestions.

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LETTERINGS OF FIGURES

- | | |
|-----------------------|--|
| 1. dvm. | Dorso-ventral muscles. |
| 2. dvom. | Dorso-ventral oblique muscles. |
| 3. eidm. | External intermediate dorsal muscles. |
| 4. eldm. | External lateral dorsal muscles. |
| 5. elvm. | External lateral ventral muscles. |
| 6. emdm. | External median dorsal muscles. |
| 7. emvm. | External median ventral muscles. |
| 8. ildm. | Internal lateral dorsal muscles. |
| 9. ilvm. | Internal lateral ventral muscles. |
| 10. imdm. | Internal median dorsal muscles. |
| 11. imvm. | Internal median ventral muscles. |
| 12. ildm ₁ | Internal longitudinal dorsal muscles. |
| 13. ilvm ₁ | Internal longitudinal ventral muscles. |

STUDIES IN INDIAN PUFFERS OR GLOBE FISHES

III. THE NERVOUS SYSTEM OF TETRODON OBLONGUS, BLOCH.

(With 5 Text Figures.)

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The nervous system of *Tetrodon oblongus* consists as in other fishes of two portions : the "Central Nervous System" consisting of the brain and the spinal cord, and the "Peripheral Nervous System" comprising the cranial, the spinal and the sympathetic nerves. It is proposed here to describe the central and peripheral nervous systems in the order outlined below :—

(1) *The Central Nervous System :—*

(A) *The Brain :*

- (a) The Fore-brain.
- (b) The Mid-brain.
- (c) The Hind-brain.

(B) *The Spinal Cord.*

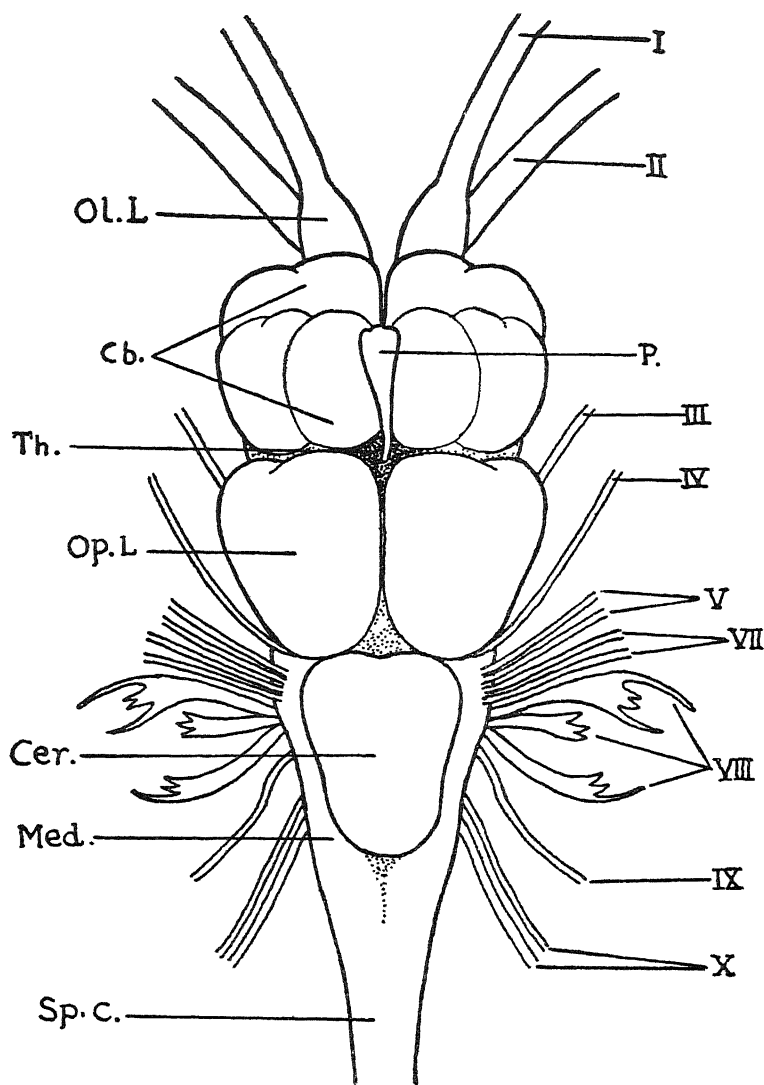
(2) *The Peripheral Nervous System :—*

- (A) The Cranial Nerves.
- (B) The Spinal Nerves.
- (C) The Sympathetic Nerves.

(1) *The Central Nervous System.*

(A) *The Brain :—*The brain of this fish is characterised by its very small size in comparison with the size of the animal and it does not fill the entire cranial cavity. It is rather short and has a rounded appearance. It can be divided as mentioned before into three parts—the fore-brain, the mid-brain and the hind-brain. (Text Figs. 1 & 2).

(a) *The Fore-brain :—*It consists of a pair of small olfactory lobes (Ol. L.), two large cerebral hemispheres (Cb.) and the thalamencephalon (Th.). The olfactory bulbs or lobes are small, solid structures, closely connected with the anterior end of the cerebral hemispheres. Apparently they seem to be the dilated bases of the olfactory nerves arising from their anterior ends. The paired cerebral hemispheres forming a large portion of the fore-brain are well developed and are dorsally separated from each other by a median

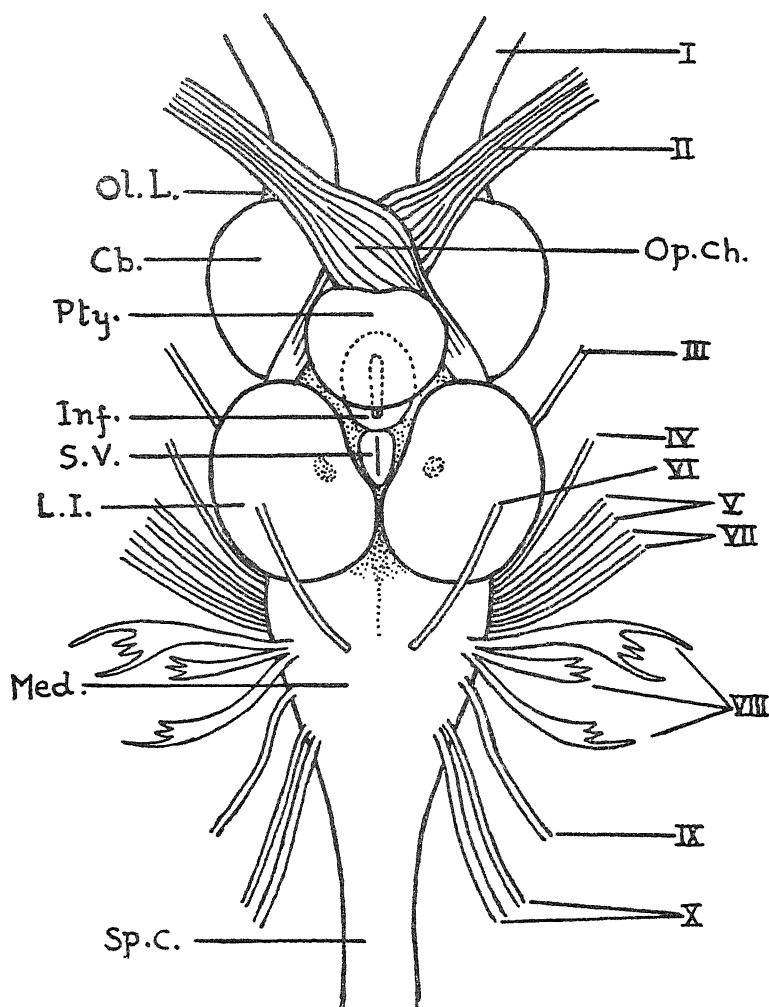


TEXT-FIG. 1 :—*DORSAL VIEW of the BRAIN of T. oblongus.*

Cb.—Cerebral hemispheres ; Cer.—Cerebellum ; Med.—Medulla oblongata ; Ol. L.—Olfactory lobes ; Op. L.—Optic lobes ; P.—Pineal body ; Sp. C.—Spinal cord ; Th.—Thalamencephalon ; I to X—Cranial nerves.

groove. They are covered over by the thin membranous pallium, which is more prominent in a preserved specimen than in a fresh one. They are broad and appear greatly lobulated on the dorsal surface. Posteriorly they almost reach the anterior margin of the optic lobes (Op. L.) and thereby conceal much of the dorsal por-

tion of the thalamencephalon. The latter, therefore, is hardly visible on the dorsal side, excepting a small median diamond shaped area, situated in between the cerebral hemispheres and the optic lobes. The epiphysis or pineal body (P.) is seen emerging out dorsally from this small region. It starts from the roof of the thalamencephalon by a slender stalk, running forwards over the pallium. It is much flattened in front and it lies over the median groove between the two cerebral hemispheres.



TEXT-FIG. 2 :—*VENTRAL VIEW of the BRAIN of T. oblongus.*

Inf.—Infundibulum ; L. I.—Lobi-inferioris ; Op. Ch.—Optic chiasma ; Pty.—Pituitary body ; S. V.—Saccus vasculosus. I to X—Cranial nerves. (Rest of the lettering as in Fig. 1.)

The thalamencephalon is, however, greatly produced vertically downwards and then backwards in the form of the infundibulum (Inf.) and other outgrowths. The hollow infundibulum descends downwards and is applied in the mid-ventral line to the pituitary body or hypophysis (Pty.). The latter develops as an outgrowth from the roof of the buccal cavity and is seen to cover a part of the optic chiasma (Op. Ch.). While the infundibulum has on its side the two lobi-inferiores (L. I.) and is produced distally into a thin-walled gland called the "Saccus Vasculosus" (S. V.). The lobi-inferiores are large bean-shaped bodies lying on the ventral side of the optic lobes. Posteriorly they touch each other along their median sides but are a little apart anteriorly and in the small area thus left between the two, is lodged the median infundibulum and the saccus vasculosus.

(b) *The Mid-brain* :—It consists of the ventral axial mesencephalon and the dorsal paired optic lobes. The former, completely covered over on the ventral side by the infundibular outgrowths, contains a vertical slit-like mesocoele and is thickened on the sides as the crura-cerebri. The optic lobes stand out prominently on the dorsal side and extend between the cerebral hemispheres in front and the cerebellum (Cer.) behind. These two large lobes are separated from each other by a median longitudinal groove. In front they are broad and are continued along the ventro-lateral sides into the optic tracts from which the optic nerves arise. The third nerve arises from the ventral side and the fourth from the dorsal side of the optic lobe.

(c) *The Hind-brain* :—The hind-brain comprises the dorsal cerebellum and the ventral medulla oblongata (Med.), gradually narrowed posteriorly into the spinal cord (Sp. C.). The elongated and rather flat cerebellum extends in front upto the optic lobes and projects over a great portion of the medulla oblongata behind. It is in fact bigger than what it appears from outside, as a part of it known as "Valvula Cerebelli" is continued anteriorly into the cavity of the mid-brain. It is quite smooth above and almost solid within. The medulla oblongata forming the last portion of the brain is a more or less triangular structure. It is broad in front and gradually narrows behind. It is very thin above but greatly thickened on the sides and on the floor. The fifth and the seventh nerves arise from its side, the eighth, the ninth and the tenth from its ventro-lateral side and the sixth from the floor of the medulla oblongata.

The Ventricles :—The central canal of the spinal cord begins to widen out near the hind end of the brain and enlarges into the large cavity of the medulla oblongata or the fourth ventricle

(metacoele). The latter is a deep and spacious cavity, covered over dorsally by a thin choroid plexus. It continues in front as the iter or aqueductus Sylvii which communicates dorsally with a very narrow and inconspicuous epicoele. The cerebellum is mostly solid in this fish and hence its cavity is practically obliterated. The iter then passes into the cavity of the mid-brain or mesocoele, communicating on each side with the cavity of the optic lobes or optocoele. The latter is somewhat reduced owing to the prolongation of the anterior part of the cerebellum into its lumen. The mesocoele runs forwards and opens below into the large third ventricle or diocoele. This cavity is prolonged downwards and backwards into the infundibulum and is thus continuous with the cavities of the lobi-inferiores and of the saccus vasculosus. Anteriorly the third ventricle leads into the median and undivided cavity of the cerebral hemispheres or the prosocoele. The latter is much reduced by the large corpora striata and is not continued forwards as the olfactory lobes are solid.

(B) *The Spinal Cord* :—The medulla oblongata is continued behind into the spinal cord (Sp. C.) which is situated in the canal formed by the neural arches of the trunk vertebræ. It is considerably short and does not reach the posterior end of the body as in other bony fishes. The remaining portion of the neural canal is therefore, occupied by the long roots of the spinal nerves, forming thereby a structure called the “Cauda Equina.” The central canal of the spinal cord is continuous (as described above) in front with the wide fourth ventricle of the medulla oblongata. The structure of the spinal cord is of the usual type found in other bony fishes and hence is not described here.

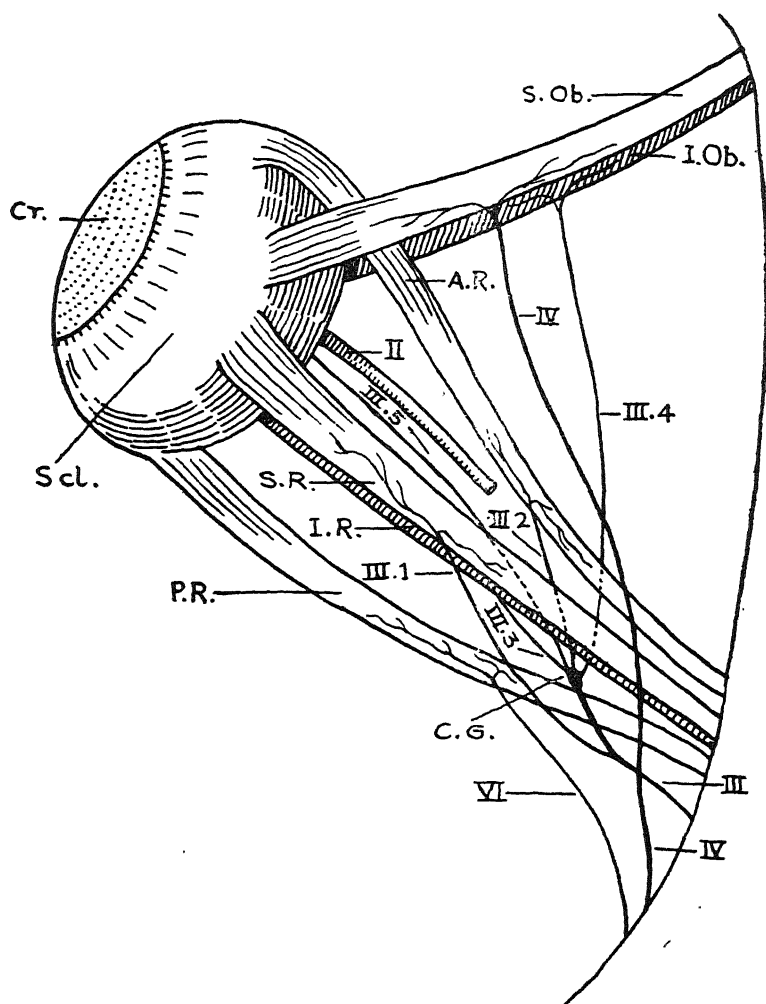
(2) *The Peripheral Nervous System* :—It consists of the cranial, the spinal and the sympathetic nerves as mentioned above.

(A) *The Cranial Nerves* :—There are ten pairs of the cranial nerves and the majority of them except the first four arises from the walls of the hind-brain.

(i) *The first or the Olfactory Nerve* :—It starts from the olfactory bulb (Text Fig. 1) and is distributed to the mucous membrane of the olfactory sac of its side. It is a purely sensory nerve. It forms a very stout and long trunk, since the nasal capsule is situated at some distance from the olfactory lobe. It leaves the cranial cavity along with the optic nerve and on its way forwards it comes to the dorsal side by traversing a big olfactory foramen in the prefrontal bone.

(ii) *The second or the Optic Nerve* :—It arises from the antero-ventral region of the optic lobe and issues out from below the olfactory lobe of the opposite side. At the beginning it has the form

of a thick ribbon with flattened ventral surface and later on it becomes cylindrical. The two optic nerves simply cross each other just above and in front of the pituitary body and the nerve from the right side of the brain goes to the left eye and from the left to the right eye. There is thus no intermingling of nerve fibres and hence the real optic chiasma is absent (Text Fig. 2.). Each optic nerve leaves



TEXT-FIG. 3 :—*EYE MUSCLES and their NERVES of T. oblongus.*

A. R.—Anterior rectus ; C. G.—Ciliary ganglion ; Cr.—Cornea ; I. Ob.—Inferior oblique ; I. R.—Inferior rectus ; P. R.—Posterior rectus ; Scl.—Sclerotic ; S. Ob.—Superior oblique ; S. R.—Superior rectus ; II—Optic ; III—Oculomotor ; III. 1. to III. 5—Branches of oculomotor ; IV—Trochlearis VI—Abducens.

V—G

the cranium through a big foramen situated in the anterior membranous part of the cranial wall and then curves outwards in the direction of the eye. Finally it perforates the sclerotic and retina and innervates the inner surface of the latter as usual.

(iii) *The Third or the Oculomotor Nerve* :—This slender motor nerve starts from the antero-ventral surface of the optic lobe and issues out in front between the optic lobe and the lobi-inferioris (Text Fig. 1). It runs for a short distance within the cranium and then passes out into the orbital region through a small foramen situated behind the optic foramen. Here it turns forwards and divides into two unequal nerves (Text Fig. 3.). The smaller branch (III. 1) runs towards the eye and breaks into the superior rectus muscle (S. R.). The bigger branch dilates into a small ciliary ganglion (C. G.) and immediately splits into four thin nerves. Three out of these (III. 2, III. 3 and III. 4) supply three eye muscles, viz., anterior and inferior recti and the inferior oblique respectively. The remaining fourth branch (III. 5) supplies the ciliary muscles of the eye and hence known as the ciliary nerve. It runs outwards mostly hidden between the superior and inferior recti muscles and then perforates the sclerotic coat (Scl.) of the eye in the vicinity of the optic nerve.

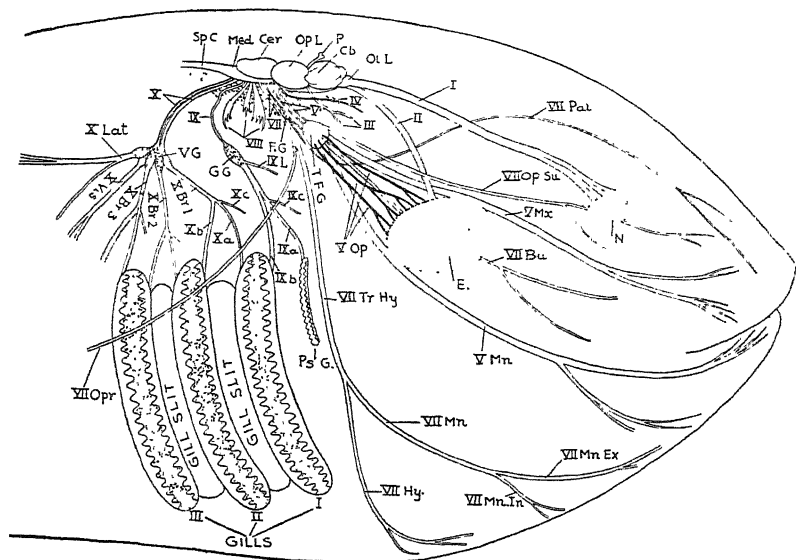
(iv) *The Fourth or the Trochlearis Nerve* :—The fourth nerve arises on the dorsal side of the brain between the optic lobes and the cerebellum (Text Fig. 1). It runs forwards within the cranium over the root of the oculomotor and then pierces the membranous wall of the brain case in front. On entering the orbital region it runs forwards dorsal to the eye muscles and optic nerve and then supplies the superior oblique muscle (S. Ob.) of the eye (Text Fig. 3).

(vi) *The sixth or Abducens Nerve* :—The sixth or the last eye muscle nerve originates from near the mid-ventral region of the medulla oblongata and runs forwards along the ventral surface of the lobi-inferioris (Text Fig. 2). It then issues out from below the brain and enters the orbit behind the third nerve. It turns forwards and reaches the posterior rectus muscle which it supplies (Text Fig. 3.).

(v & vii) *The Fifth or the Trigeminal and the Seventh or the Facial Nerves* :—The trigeminal and the facial nerves start very near each other and their branches give rise to the trigemino-facial complex (Text Fig. 4). They arise from the antero-lateral side of the medulla oblongata by four root-lets, two for each nerve. They lie very close together and leave the cranial chamber through a trigemino-facial foramen situated on the anterior side of the pro-otic bone.

The two root-lets of the trigeminal nerve dilate into the irregular and complex trigemino-facial ganglion (T. F. G.) situated just

outside the foramen. The first or upper root-let of the facial dilates itself into a small facial ganglion (F. G.) within the cranium and then joins the common ganglion. The other lower root-let of the seventh runs out closely opposed to the facial ganglion but separates from the other root on emerging out of the cranium.



TEXT-FIG. 4 :—Side VIEW of the CRANIAL NERVES of *T. oblongus*.

E.—Eye; F. G.—Facial Ganglion; G. G.—Glossopharyngeal ganglion; N.—Nostril; Ps. G.—Pseudo-gill; T. F. G.—Trigeminofacial ganglion; V. G. Vagus ganglion; V. Mn.—Mandibularis; V. Mx.—Maxillaris; V. Op.—Ophthalmic nerves; VII Bu.—Buccalis; VII Hy.—Hyoideus; VII Mn.—Mandibularis; VII Mn. Ex.—Mandibularis externus; VII Mn. In.—Mandibularis internus; VII Opr.—Opercularis; VII Op. Su.—Ophthalmic superficialis; VII Pal.—Palatinus; VII Tr. Hy.—Truncus Hyomandibularis, IX a.—Pre-trematic branch; IX b.—Post-trematic branch; IX c.—Pharyngeal branch; IX L.—Lingual; X a.—Pre-trematic branch; X b.—Post-trematic branch; X. c.—Pharyngeal branch; X Br¹ to X Br.³—Branchial nerves, X Lat.—Lateralis; X Vis.—Visceralis; (Rest of the lettering as in Fig. 1.).

The *Trigeminal nerve* consists of the following branches :—(1) Three Ophthalmic Nerves, (2) the Maxillaris, and (3) the Mandibularis.

The usual Ophthalmicus Superficialis branch of the trigeminal generally found running parallel with a similar branch of the facial in other fishes is not found in this fish. It might have either intimately fused with that of the facial or might have shortened and

changed its course. The latter view seems to be more probable in this case. For there is found a group of three short nerves arising from the dorsal side of the ganglion, just above the origin of the maxillaris and mandibularis branches. These three nerves which lie dorsal to all other nerves run towards the external margin of the eye. They supply the skin and sense organs above the eye and are named as *Ophthalmic Nerves* (V Op.).

The Maxillaris branch (V Mx.):—It arises from the antero-ventral part of the compound ganglion along with the mandibularis branch of the same nerve. It forms a flat ribbon-like nerve, running forwards along the upper margin of the floor of the orbit, ventral to the eye muscles. It runs directly towards the upper jaw and then divides into two unequal branches. The smaller of the two turns towards the dorsal side and supplies the skin of the snout behind the upper jaw. The other stout branch passes through a foramen in the maxilla and comes to the anterior side of the jaw. Here it breaks into several branches supplying the upper jaw, the skin and sense organs of the snout.

The Mandibularis branch (V Mn.):—This separates from the maxillaris soon after its origin and likewise develops into a stout ribbon-like nerve. It lies ventral to the eye ball and runs obliquely forwards along the outer margin of the floor of the orbit. Behind the angle of the jaw it gives off a small ventral branch which descends down and supplies the skin and the muscles on the lower side. The main trunk however turns forwards and emerges in front of the lower jaw by passing through a foramen in the dentary. Here it lies immediately beneath the skin and divides into a number of branches supplying the skin, the sense organs and other parts of the lower jaw.

The Facial nerve is made up of the following branches :—
(1) the Ophthalmicus Superficialis (2) the Buccalis (3) the Palatinus (4) the Opercularis Superficialis (5) the Mandibularis consisting of Mandibularis Externus and Mandibularis Internus and (6) the Hyoideus.

The Ophthalmicus Superficialis facialis (VII Op. Su.) starts from the dorsal side of the complex ganglion and extends along the upper border of the orbit. It passes forwards dorsal to other nerves and gives a few branches to the sense organs near the eye. The main nerve bends upwards near the nostril and then runs forwards along the dorsal side of the snout. Here it divides into several branches supplying the sense organs and the skin of that region of the snout.

The Buccalis nerve (VII Bu.) is seen to enter the orbit along with the maxillary and mandibular branches of the fifth. It im-

mediately separates from them and continues across the floor of the orbit, dividing into two branches. The dorsal of the two runs ahead almost parallel to the maxillaris of the fifth and supplies the sense organs of the snout. The other ventral branch descends downwards to supply the infraorbital canal.

The Palatinus branch (VII Pal.) arises as a slender nerve from the ventral side of the facial ganglion. It runs forward along the orbit ventral to other nerves and the eye muscles. It slowly courses upwards and issues on the dorsal side by passing below the olfactory nerve. It then runs forwards and downwards by piercing the vomer and the upper jaw. It finally reaches the buccal cavity where it sends branches to its roof and to the membrane lining the upper jaw internally.

The other ventral root-let of the facial separates from the facial ganglion and runs downwards and outwards. At its beginning it gives off posteriorly a branch known as the *Opercularis Superficialis* (VII Opr.). The latter obliquely runs behind upto the edge of the operculum and supplies the latter and the sense organs of that region. While the main trunk running downwards as the *Truncus Hyomandibularis* (VII Tr. Hy.) gives off anteriorly the *Mandibularis* of the seventh (VII Mn.) and then continues straight downwards as the *Hyoideus nerve* (VII Hy.). The mandibularis branch turning forwards, gives off at some distance a small *Mandibularis Internus* (VII Mn. In.) and then passes forwards as the *Mandibularis Externus* (VII Mn. Ex.). The Mandibularis Internus immediately passes down and supplies the mucous membrane, while the Mandibularis Externus extends forwards and breaks into the skin and the sense organs of the hyomandibular canal. Lastly the Hyoideus nerve continues downwards and then forwards, and divides to supply the sense organs and muscles of that hyomandibular region.

(viii) *The Eighth or the Auditory Nerve* :—This nerve arises from the medulla apparently by three root-lets, situated close behind the fifth and seventh nerves. Each root-let widens into a short flattened branch which divides into fine twigs at its extremity. The most anterior branch which is stouter and longer of the three, turns forwards to supply the ampullae of the horizontal and anterior vertical semicircular canals. The middle or the central one is a short branch, breaking into the utriculus. While the third or the most posterior branch runs backwards and outwards to supply the sacculus, the legena and the ampulla of the posterior vertical semicircular canal.

(ix) *The Ninth or the Glosso-pharyngeal Nerve* :—It starts from the ventro-lateral border of the medulla oblongata by a single root and passes behind obliquely (Fig. 4.). It bends outwards and then issues out of the cranial cavity through a foramen in the ex-occipital bone. After its exit it courses forwards and downwards and swells into the elongated glossopharyngeal ganglion (G.G.). It then leaves the ganglion as a flat trunk running downwards up to the region of the first gill-cleft. Here it divides into a slender pre-trematic branch (IX a) and a large post-trematic branch (IX b). The former first gives off anteriorly a pharyngeal branch (IX c) and then passes forwards to the pseudo-gill (Ps.G.). The small pharyngeal branch goes down to supply the pharyngeal muscles and the mucous membrane of that region, while the post-trematic nerve runs backwards to the first branchial arch to supply the anterior demibranch of the first gill. Lastly a lingual nerve (IX L.) starts from the lower end of the glossopharyngeal ganglion and passes downwards and forwards to supply the mucous membrane of the mouth.

(X) *The Tenth or the Vagus Nerve* :—This last cranial nerve leaves the medulla by two root-lets, situated just behind the root of the ninth (Fig. 4). The two root-lets of which the upper one is smaller, run backwards and leave the cranium by the vagus foramen found in the ex-occipital bone. They then fuse together into the compound vagus ganglion (V.G.), composed of five small ganglia, situated close together. From the latter arise the three Branchials, the Visceralis and the Lateralis nerves.

The First Branchial Nerve (X Br. 1):—This most anterior branch of the vagus continues forwards from its ganglion as a flat nerve and then turns outwards in the direction of the first branchial arch. Here it divides into a smaller anterior and a larger posterior branch. The former gives off at its beginning a small pharyngeal branch (X c) and then runs as a pre-trematic branch (X a) to the posterior demibranch of the first gill. The pharyngeal descends downwards to supply the branchial muscles and the mucous membrane of the pharynx. While the other branch known as the post-trematicus (X b) turns behind and runs outwards to the second branchial arch to supply the anterior demibranch of the second gill.

The Second Branchial Nerve (X Br. 2.):—Like the first it starts from its ganglion and runs outwards and downwards towards the second branchial arch. It on its way splits into the usual pre-trematic and post-trematic branches. The former after giving the pharyngeal to that region of the pharynx goes to the posterior demibranch of the second gill. The latter or post-trematicus runs

behind to the third branchial arch in order to supply the anterior demibranch of the third gill.

The Third Branchial Nerve (X Br. 3.):—This third branchial trunk runs downwards from its ganglionated beginning and soon splits into two nerves, the anterior or pre-trematic branch like the two previous ones gives the pharyngeal to the pharynx and then goes to the posterior demibranch of the third gill. The large posterior branch, corresponding to other post-trematics runs downwards and backwards. It then divides into smaller branches descending down to supply the oesophagus, the pharynx and the branchial arches.

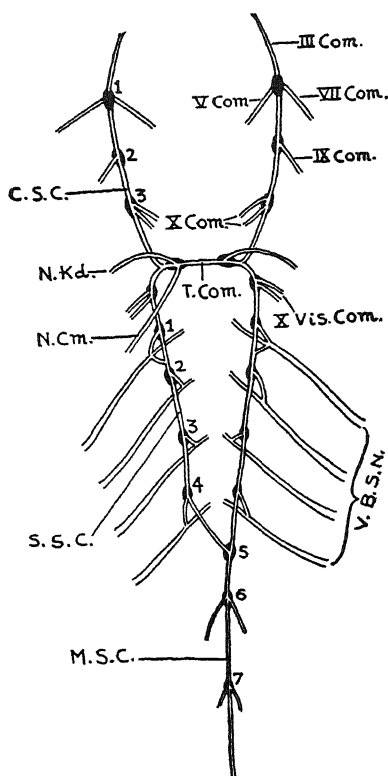
The Visceralis Nerve (X Vis.):—This is a large branch arising from the ventral side of the vagus ganglion. It issues out posteriorly from its ganglion and runs backwards as a flat nerve trunk. It turns downwards and enters the body cavity. It then passes behind and gives off several branches to supply the internal viscera.

The Lateralis Nerve (X Lat.):—This is the most dorsal and posterior branch of the vagus. Immediately on leaving the ganglion it forms a large nerve trunk, running backwards between the body muscles. It gives off a little behind its commencement a small branch to the pectoral region and then proceeds backwards giving off numerous small branches to the sense organs of the lateral line canal.

(B) *The Spinal Nerves*:—These paired nerves arise from the sides of the spinal cord and correspond in number with the number of the vertebræ. As in a typical bony fish each spinal nerve starts by two roots—a dorsal sensory and a ventral motor root. Both the roots run backwards within the neural canal and unite into a common nerve trunk. The latter leaves the canal through a foramen in the neural arch and immediately swells into a single extra-vertebral ganglion. The usual dorsal and ventral branches are given off from the ganglion to supply the dorsal and ventral muscles respectively. As the spinal cord is considerably short, the posterior spinal nerves have to travel a long distance within the neural canal before they come out from the corresponding vertebræ.

(C) *The Sympathetic Nerves*:—The sympathetic nervous system (Text Fig. 5) consists more or less of two longitudinal nerve cords or trunks bearing sympathetic ganglia at intervals. They run ahead on each side of the vertebral column and then enter the cranium. The two cords run behind for some distance and then unite into a single cord ending in the haemal canal of the tail. Each cord can be conveniently divided into a cranial sympathetic section

(C. S. C.) associated with certain cranial nerves and a spinal section (S. S. C.) associated with some spinal nerves.



TEXT-FIG. 5 :—The SYMPATHETIC NERVOUS SYSTEM of *T. oblongus*.

C. S. C.—Cranial Sympathetic Cord ; M. S. C.—Median Sympathetic Cord ; N. Cm.—Nerve running along the Coeliaco-mesenteric artery ; N. Kd.—Nerve to the Kidney ; S. S. C.—Spinal Sympathetic Cord ; T. Com.—Transverse Commissure ; V. B. S. N.—Ventral Branches of the Spinal Nerves ; III Com., V Com., VII Com., IX Com., and X Com.—the connecting branches to the respective cranial nerves ; X Vis. Com.—connecting branch to the Visceralis. (The numbers represent the sympathetic ganglia).

The cranial sympathetic trunk of each side bears three ganglia and is connected with five cranial nerves by means of connecting branches. Three of these (III Com. V Com. & VII Com.) arise from the first ganglion and are connected with the third, the fifth and the seventh cranial nerves respectively. A single small nerve (IX Com.) arising from the second ganglion goes to the glosso-pharyngeal ganglion and two similar branches (X Com.) are sent

to the vagus from the third ganglion. Posteriorly the two cranial cords are connected with each other by a short transverse commissure (T. Com.), situated at about the junction of the skull with the vertebral column. This commissure has two ganglia, one on each side. The ganglion on the right side gives off two nerves, one supplying the kidney (N. Kd.) and the other running along the coeliaco-mesenteric-artery (N. Cm.), while the left sends only one nerve to the kidney of its side.

A little behind the transverse commissure each cord swells into the visceralis ganglion from which two small nerves (X Vis. Com.) are sent to the visceralis branch of the tenth nerve. As the spinal sympathetic cord of each side continues backwards along each side of the aorta, it bears four sympathetic ganglia. Each of them sends a branch which is connected with a ventral branch of the corresponding spinal nerve (V.B.S.N.). An additional communicating branch arising from the cord also goes to the ventral branch of the second spinal nerve. In the region just behind the fourth vertebra the right sympathetic trunk passes across the vertebral column to unite with the left one and then dilates into a big ganglion at this junction.

Behind this region the spinal sympathetic system is continued as a median unpaired cord (M.S.C.). The latter bears at intervals small ganglia from which paired connecting nerves are sent to the ventral branches of the spinal nerves in the following few vertebræ. Further behind, the common trunk becomes very slender and inconspicuous and continues into the haemal canal of the tail.

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STUDIES IN GLYCOLYSIS OF BLOOD IN VITRO.

By

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The study of glycolysis in blood has attracted several workers. From 1876 until the present time attempts have been made to elucidate the factors involved in glycolysis. A large amount of work has been done but there seem to be no definite conclusions drawn.

It has been known from the time of Claud Bernard (1876) that shed blood loses its sugar on standing, and Spiro in 1877 found lactic acid in blood. The amount of lactic acid increases on standing (Fries : 1911) and with increase in the concentration of lactic acid there is a corresponding decrease in glucose (Kraske : 1912; Kondo: 1912; Evans: 1922.) Margulis and Barkus (1925) have shown that the disappearance of sugar runs parallel with the formation of lactic acid while other workers (Collazo & Morelli: 1926 ; Partos & Herzog : 1930) report that no such relationship exists. Altman (1927) suggests that some intermediary substance with a lower reducing power than glucose is formed, before glucose is finally converted into lactic acid ; while Bierry and Moquet (1925) assume the temporary formation of a hexosephosphorous compound. Lundsguard & Holboel (1925) ascribe the process of glycolysis to an enzyme which is present in the red corpuscles but not in plasma, while some workers have found that glycolysis occurs in plasma. Aibara (1922) suggests that white cells produce glycolytic enzymes. Kawashima (1922) suggests that glycolysis of the blood is entirely due to erythrocytes.

Thus the results of various workers are conflicting and it may be due to the diversity of the methods employed for the estimation of lactic acid and also due to the blood studied being from different species. It is reported that the glycolysis varies in the blood of individuals of the same species at different periods. An attempt to correlate the results obtained from the blood of dog, cat, sheep, horse, man, etc. has not met with success. Glycolysis in blood seems to be more complicated than the process of formation of lactic acid in the contraction of muscle.

It is proposed to study the defibrinated horse blood throughout this investigation to avoid the disturbing factors, if any, due to the use of blood from different animals. Without going into the mechanism or the factors influencing glycolysis which will be taken up later, the present work aims at locating the seat of glycolysis in the different elements of the blood, and at finding out the relationship that may exist between sugar and lactic acid.

EXPERIMENTAL METHODS

Blood was drawn aseptically from the jugular vein of a horse into a sterilized flask and was defibrinated by glass beads contained in it. For the study of glycolysis defibrinated blood is more suitable than whole blood since the anti-coagulants used have an inhibitory effect on glycolysis. In dealing with defibrinated blood it is important to shake the flask evenly to get a homogeneous mixture of corpuscles and plasma and at the same time to prevent the rupture of the corpuscles. Several such precautions were taken during the work.

Lactic acid was estimated by Clausen's (1922) method as modified by Cotonio, Friedemann, and Shaffer (1927), the distillation being carried out without aeration (personal communication : May-erhof). The proteins were precipitated by 40 per cent. trichlor-acetic acid and the reducing sugars were removed from the protein-free filtrate by the method of Van Slyke (1917).

The blood sugar was determined by the method of Hagedorn and Jensen (1923). Both lactic acid and sugar estimations were carried out in duplicate.

Analyses of lactic acid and sugar were carried out at the temperature of the refrigerator, viz. 8°C, and at the room temperature, viz. 30° C in water bath maintained at that temperature. The glycolysis at the refrigerator temperature is slow and consequently more convenient to follow the changes; the hæmolysis occurring only after a very long time.

RESULTS

Table I gives the results of analyses of the defibrinated blood at the above temperatures.

TABLE I.

No. of hrs.		Lactic acid in mgs/100 ml.	Sugar in mgs/100 ml.
Analysis of blood at the temperature of 8°C.			
1.)	0	10.78	...
	2.5	22.65	128.3
	25	50.12	126.6
	55	60.47	114.6
	119	65.18	70.8
2.)	0	34.31	...
	2	35.21	162.0
	18	38.70	161.3
	26	47.36	161.3
	48	47.84	159.3
3.)	0	30.73	129.2
	3	32.99	128.3
	5	43.96	123.9
	18	46.16	97.4
4.)	0	30.51	141.7
	3	— —	139.8
	7	43.07	132.7
	19	44.41	125.7
	46	67.41	111.5
	80	70.45	110.3
5.)	6	34.88	123.9
	18	45.63	106.2
	42	50.29	92.9
	66	65.61	79.7
6.)	2	32.85	132.7
	8	44.89	129.9
	18	50.79	119.5
	28	59.49	116.8
	42	62.21	110.6
	66	64.68	92.9
	89	65.96	79.6
7.)	10	27.86	115.0
	23	32.50	110.6
	33	43.77	88.5
8.)	2	31.20	102.7
	18	51.80	102.2
	26	51.33	97.3
	50	57.36	79.6
	74	63.17	70.0
	98	70.26	47.0

No. of hrs.	Lactic acid in mgs/100 ml.	Sugar in mgs/100 ml.
Blood analysed at the temperature of 30°C.		
9) 2	33.98	130.1
6	45.92	106.2
22	65.45	65.3
27	85.84	48.1
10) 2	31.99	150.4
6	49.49	109.7
22	63.81	73.1
11) 2	31.20	102.7
16	69.33	52.5
24	80.63	39.4
12) 3	32.44	154.4
6	45.55	119.5
23	81.44	67.8
29	89.47	37.6

It will be seen from the above results that the concentration of lactic acid increases rapidly in the early stages while the fall in the concentration of sugar is less marked. But in the final stages of glycolysis the fall in the sugar concentration is considerable while there is no corresponding rise in the concentration of lactic acid. It is also seen that the concentration of sugar does not fall to zero even though the blood is allowed to stand up to the point where hæmolysis occurs.

The suggestion by Konign (1921) that sugar increases after 24 hours is thus not confirmed by the above results.

In order to study the course of glycolysis in (i) serum and in (ii) corpuscles, defibrinated blood was centrifuged for an hour and the serum was carefully removed. The corpuscles were freed completely from the serum and were used in this study.

Table II gives the results of analyses carried out with the serum obtained from the defibrinated blood at the temperatures 8° C, and 30° C.

TABLE II.

No. of hrs.	Lactic acid in mgs/100 ml.	Sugar in mgs/100 ml.
Serum analysed at the temperature of 8° C.		
1) 0	48.55	141.6
34	55.52	139.7
55	57.34	137.0
2) 0	32.61	166.4

No. of hrs.		Lactic acid in mgs/100 ml.	Sugar in mgs/100 ml.
3)	10	53.59	164.6
	20	53.31	152.8
	34	56.64	152.2
	0	33.11	132.7
	12	36.87	123.9
	36	36.52	88.5
4)	60	37.83	84.0
	0	48.19	130.1
	16	54.17	118.6
	20		106.2
Serum analysed at the temperature of 30° C.			
5)	0	40.77	149.6
	9	42.85	141.6
	25	48.55	139.6
6)	0	31.02	172.6
	9	35.50	166.4
	25	43.07	159.0

It is seen that the glycolysis in serum is less rapid than in blood. There is an appreciable rise in the concentration of lactic acid while there is no corresponding fall in the concentration of sugar. This phenomenon is the same as in the early stages of glycolysis in blood. The statement of Aibara (1922), Katayama (1926) and Kawashima (1922) that glycolysis is absent in the serum is not confirmed.

Table III gives the results of analyses carried out with the corpuscles obtained from the defibrinated blood. In the following experiments, great care was taken to keep the corpuscles intact.

TABLE III.

No. of hrs.		Lactic acid in mgs/100 ml.	Sugar in mgs/100 ml.
Corpuscles analysed at the temperature of 8° C.			
1)	0	28.4	98.7
	5	30.1	82.8
	10	36.6	61.2
	24	42.8	47.0
Corpuscles analysed at the temperature of 30° C.			
2)	0	33.90	97.6
	4	34.97	61.2
	27	37.87	54.2
	48	40.18	49.0

No. of hrs.	Lactic acid in mgs/100 ml.	Sugar in mgs/100 ml.
3) 0	45.71	76.1
4	51.57	64.7
27	95.85	49.0
4) 0	34.8	97.3
4	39.3	88.5
10	45.2	76.1
24	58.9	61.2

It is seen that the glycolysis in the corpuscles is rapid. While there is an increase in the concentration of lactic acid there is a corresponding or even greater fall in the sugar concentration, as in the later stages of glycolysis in blood.

The corpuscles obtained from the defibrinated blood were suspended in an isotonic solution (0.9 % NaCl) and the volume made up to the original blood so that the percentage of corpuscles in the system remained the same as that of blood.

Table IV gives the result of analyses carried out with the corpuscles suspended in an isotonic solution.

TABLE IV.

No. of hrs.	Lactic acid in mgs/100 ml.	Sugar in mgs/100 ml.
Analysed at the temperature of 8° C.		
1) 0	11.58	47.8
34	11.88	26.2
55	12.83	15.4
2) 0	18.14	35.0
10	18.80	32.0
20	19.51	26.2
34	20.76	21.9
3) 0	20.25	30.6
12	20.61	26.25
36	22.42	21.9
Analysed at the temperature of 30° C.		
4) 0	26.37	29.2
9	26.89	20.1
25	32.93	19.2
5) 0	27.32	84.0
48	30.46	61.2

It is interesting to note that in this case the lactic acid concentration increases very slowly while there is a marked fall in the

sugar concentration. It is suggested by Kawashima (1922) that the glycolysis is almost entirely due to the corpuscles. It is seen from the above that in the absence of serum the glycolysis is not as rapid as in blood. This result is in agreement with those of Aibara and Kawashima who have found that the glycolytic activity of erythrocytes in physiological salt solution is less than that in the serum.

SUMMARY AND CONCLUSIONS

- 1) In the early stages of glycolysis of the blood the rise in the concentration of lactic acid is rapid while the fall in the concentration of sugar is less marked; whereas in the later stages the changes are in the reverse order. The sugar does not completely disappear.
- 2) The glycolysis in serum is less rapid than in blood or in the corpuscles but the statement of other workers that it is absent in serum is not confirmed. It is also noticed that there is an appreciable rise in the concentration of lactic acid while the sugar concentration does not fall to the same extent. This phenomenon is the same as in the early stages of glycolysis in blood.
- 3) The glycolysis in the corpuscles is rapid. While there is an increase in the concentration of lactic acid, there is a corresponding or even greater fall in the sugar concentration, as in the later stages of glycolysis in blood.
- 4) Glycolysis in the corpuscles suspended in isotonic solution is not rapid as in blood.
- 5) Both components—serum and corpuscles—are necessary for glycolysis.

Investigation of other factors in the mechanism of glycolysis is in progress.

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THE PROBLEM OF NUTRITION IN INDIA

By

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[A paper read before a joint meeting of the Sections of Medical and Veterinary Research, Physiology, Agriculture and Chemistry, Indian Science Congress—Hyderabad, Deccan, January 1937].

I.

A Joint session such as this, and particularly of the sections of Medical and Veterinary Research and of Agriculture to discuss the problem of Nutrition is to be welcomed. It was Mr. Bruce, the Australian Delegate to the League of Nations Assembly, who once used the happy phrase 'Marriage of Agriculture to Public Health' for such a consummation as we witness here to-day. I trust this marriage will endure and will be happy and prosperous.

The problem of nutrition in this Country is a complex one. But it is a gratifying sign of the times, that the people are becoming *nutrition-minded*. Like air-mindedness, nutrition-mindedness has come rather slowly, but I hope, surely. There is no denying the fact that good health depends on good nutrition, and for those entrusted with the task of maintaining at a high standard the Public Health of the Community, the problem of nutrition forms or should form, the first item of their programme of work. But the task of the Public Health worker would be impossible without the active co-operation of the Agriculturist, who has to provide the necessary articles of diet for the people.

I need hardly emphasise the fact, that the standard of nutrition in this country is very low. The diet of the large majority of the inhabitants is poor in protein and fat and inadequate as regards certain Vitamins and minerals. Apart from poverty, which undoubtedly is an important factor, the diet here is regulated largely by custom, tradition and religious sanction, which make the task of the reformer

and the public health worker extremely difficult. It is hard to convince people that custom and religious sanction, not to speak of instinct and appetite, are not and cannot be regarded as reliable guides to the choice of food. The obvious remedy lies in educating the people in the principles of Dietetics, and in providing necessary articles of diet at prices which they can well afford.

II.

As you know, the League of Nations has taken up the question of Nutrition seriously. This is as it should be. The subject is world wide in its scope and outlook. The Assembly of the League in 1935, adopted the following resolution :—

‘The Assembly, having considered the subject of nutrition in relation to public health and of the effects of improved nutrition on the consumption of agricultural products, urges Governments to examine the practical means of securing better nutrition and requests the Council :

- (i) To invite the Health organisation of the League of Nations to continue and extend its work on nutrition in relation to public health.
- (ii) To instruct the technical organisations of the League of Nations, in consultation with the International Labour Office and the International Institute of Agriculture, to collect, summarise and publish information on the measures taken in all countries for securing improved nutrition ; and
- (iii) To appoint a Committee, including agricultural, economic and health experts, instructed to submit a general report on the whole question, in its health and economic aspects to the next Assembly, after taking into consideration, *inter alia*, the progress of the work carried out in accordance with paragraphs (i) and (ii) above.’

As the result of enquiries based on this resolution the following four publications have been issued by the League very recently (1936), which are of profound interest and should be read with care by all interested in the subject of nutrition :—

- (a) Vol. I. Interim Report of the Mixed Committee on the Problem of Nutrition under the Chairmanship of Viscount Astor.
- (b) Vol. II. Report on the Physiological basis of nutrition drawn up by the Technical Commission of the Health

Committee under the Chairmanship of Professor Edward Mellanby, Secretary-General of the Medical Research Council.

- (c) Vol. III. Nutrition in various countries.
- (d) Vol. IV. Statistics of Food Production, Consumption, and Prices.

The reports deal with enquiries made in Europe and in Countries of Western Civilization. They do not describe the conditions prevailing in the Far East, Asia and Africa, but arrangements for investigations in these countries have already been started by the League Health Organisation. We shall await their report on India with deep interest. But in the meantime we may glance at the reports that are already available, and see how far they can be of help to us.

I. The foods are divided by the Mixed Committee into two classes :—

- (a) *Protective Foods*, comprising products of dairy farming, of market garden and the fishing industry, such as meat, eggs, fresh milk, fresh vegetables, fresh fruit. They supply 'good' protein, vitamins and mineral salts.
- (b) *Non-Protective Foods* comprising proteins, fats, carbohydrates, such as meat, legumes, cereals, sugar, butter and oils, etc. They are valuable as providers of energy (Calories).

Lack of protective foods causes various 'deficiency' diseases, while the lack of non-protective foods causes starvation.

In India malnutrition is due to lack of both these types of food. Lack of good 'protein' is probably the cause of poor nutrition of the classes which are habitually vegetarians, while chronic under-nutrition is probably due to deficiency of Caloric requirements. The diet of even the well-to-do classes is often incomplete and sub-optimal in value. Frank evidence of dietetic inadequacy consists of course in detecting cases of rickets, Scurvy, Beri-Beri, poor musculature, poor teeth, nutritional anæmia, xerophthalmia, Chronic fatigue, poor condition of skin, sub-normal growth, and sub-normal weight. This evidence is by no means lacking in India.

I would like to draw the attention of this gathering particularly to the enormous amount of ill-health in pregnant and nursing mothers, due to improper and incomplete diet in many parts of

India. Osteomalacia amongst them is not an uncommon malady. It is probably late Rickets due to lack of vitamin D. This aspect of the problem needs immediate attention. They need abundant supply of good milk, apart from other articles of diet.

Not the least important is the problem of nutrition in infancy and early childhood. The report rightly calls it the *Kernal of the Problem*. Here again the proper supply of milk is the chief desideratum. We must have a comprehensive scheme of good milk supply to the school children, in which municipalities and private benefactions should play an important part.

The report says: 'Pregnant women, nursing mothers and young children must be considered from a nutritional standpoint as the most vulnerable portion of the population, in the sense that damage inflicted in childhood by bad food cannot be subsequently repaired. It is definitely established that many of the ill-effects which result from insufficient diet in childhood, such as rickets, bad teeth, and nutritional anæmia are avoidable by adequate provision of ordinary foods, the most important of which is milk.'

Suitable dietetics in the young are a *preventive aspect* of our work. 'Remedial treatment for the older age groups, who must often be regarded as 'damaged goods,' must also have its place in the planning of a nutritional campaign, but it is the preventive rather than the curative aspect of the problem which should be given the first place. From a national standpoint, the cost of the investment so made in the health of the children will be more than compensated by the improved vigour and physique of the adult population.'

The ignorance of the knowledge of dietetics is a lamentable fact. This ignorance is confined not only to the uneducated, but exists also, I am afraid, amongst the educated classes.

While I strongly support every possible good scheme for research work on nutrition in India, I also strongly hold that wide propaganda and extensive educational work on the subject are of prime importance. A knowledge of dietetics should be imparted in schools and colleges. The instruction should be as simple and practical as possible. The Universities should organise extramural instruction on the subject for the benefit of the adult population. By means of the Magic Lantern, the Cinema, the Radio and the Press the knowledge of proper dietetics should be brought home to the people. The scientist has far too long been living a life of

proud seclusion. It is high time that the valuable knowledge gained by patient research should be broadcast for the welfare of the people.

In such propaganda we do not aim at a uniform system of diet for all. There is a great variety of articles from which the daily menu can be chosen in such a way, that it will satisfy the special habits and religious sanctions of the people. May I invite your attention to the following remarks in the report :—

‘The objective must be not to attempt to prescribe a single type of diet for all the peoples of Europe and other countries of Western civilization, but to promote the development of agricultural production along the lines, which science makes possible, having regard to the differences of soil, climate, etc., with a view to providing the most efficient food supply taking into consideration the traditional dietary of the people.’

III.

The ‘Mixed Committee’ supplies us with a very valuable table giving the nutritive value of foods. It contains a rough classification of some of the common types of foods into protective and non-protective foods, and shows their relative value as vehicles of energy, good protein, minerals, and the more important vitamins. The only criticism I have to make about this Table is that legumes (dry peas and lentils) which are largely consumed in India, do possess high energy and caloric value and do contain a certain amount of ‘good’ protein. I suggest that the Letter E be placed next to this item and one ⊥ sign entered against it under the column ‘good protein.’ Mottram⁶ also suggests that it would be well if E were prefixed to cheese and legumes, and that a plus sign should appear under Vitamin C in the line dealing with liver, and under minerals in the line dealing with fat fish, the flesh of which contains potassium phosphate and unavoidable bones contain calcium phosphate. I agree with him. The Table as modified by Mottram and me is as follows :—

NUTRITIVE VALUE OF FOODS

Food.	"Good" protein	Minerals	Vitamins				
			A	B	C	D	
Milk	++	+++	+	+	+φ	+φ	Highly protective foods.
E Cheese	++	++	+	+	—	—	
E Eggs	++	++	+	++	—	++	
E Liver	++	++	+	++	+	+	
E Fat Fish Herrings etc.	+	+	+	+	—	++	
Green Vegetables, Salads, Raw fruits, fruit juices.	+	+++	+	+	++	—	
		+++	+	+	++	—	
E Butter	—	—	+	—	—	+φ	
E Cod liver oil	—	—	+++	—	—	+++	
Yeast	+	+	—	++	—	—	
Meat (Muscle) Root vegetables (tubers)	+	⊥	—	+	⊥	—	Less protective and non-protective foods.
			+	+	+	—	
E Legumes (dry peas, lentils).	⊥		—	+	—	—	
E Cereals, bread (whole meal).	+	⊥	⊥	+	—	—	
E Cereals, bread (white)			—	—	—	—	
E Cereals, rice (polished)			—	—	—	—	
E Nuts	⊥		—	++	—	—	
E Sugar, Jam, honey			—	—	—	—	
E Margarine, olive oil and other vegetable oils.			—	—	—	—	

E Foods of high energy or caloric value.

+++ Signifies very rich.

++ Signifies rich.

+ Signifies present.

⊥ Signifies present in small amount or traces.

— Signifies absent

Ø Signifies in summer, when the cows are on pasture.

* Signifies, if yellow in colour.

(League of Nations: The Problem of Nutrition: Vol. I. Interim Report of the Mixed Committee on the problems of Nutrition. Table regarding Nutritive value of Foods as modified by Bhatia and Mottram.)

The report dealing with the physiological basis of nutrition gives the caloric requirements for adults and other age groups, and 'supplements' for muscular activity as well as for the requirements for pregnant and nursing women. It also gives valuable data regarding protein, fat, mineral, and vitamin requirements. This information is given in a simplified form and is very useful.

IV.

A large number of problems dealing with nutrition await solution ; but I may mention three which need to be attended to :—

1. The influence of tropical climate on food requirements.
2. The intervals at which food should be taken. This has an important influence on industrial output and a sense of physical well-being and vigour. There are certain experiments of H. W. Haggard and L. A. Greenberg in America, which show that for the working man or woman as for the active growing child the highest efficiency and vigour require not more food but food in smaller amounts at more frequent intervals. This aspect of the problem has hitherto been neglected.
3. *Vegetarianism.* a large proportion of our countrymen live on a purely vegetarian diet. Systematic investigations are necessary to appraise the precise influence of vegetarianism on body nutrition and the direction in which improvement should be made.

For progress on a nation-wide scale in regard to human nutrition in this country a concerted effort on the part of the people and the Government is necessary. A central supervising authority, which will co-ordinate the work done by research organizations, the educational work of the Universities, schools, and popular instruction as well as work on the economic side 'so that measures effecting supply of food are brought into harmony with nutritional requirements' is essential. In England such central body is the advisory Committee on Nutrition responsible to the Minister of Health and the Secretary of State for Scotland. In India we are glad to see that there is the Nutrition Advisory Board attached to the Indian Research Fund Association. This and the Indian Nutrition Committee of the Indian Science Congress and the Imperial Council of Agricultural Research should co-operate with each other. We can thus look forward to a comprehensive policy of Nutrition in the near future, which will result in a *healthier, stronger*, and let us hope, a *happier* and more prosperous India.

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THE SKELETON OF HARPODON NEHEREUS (HAM. BUCH.)

(I) THE SKULL

(with 14 Text-figures)

By

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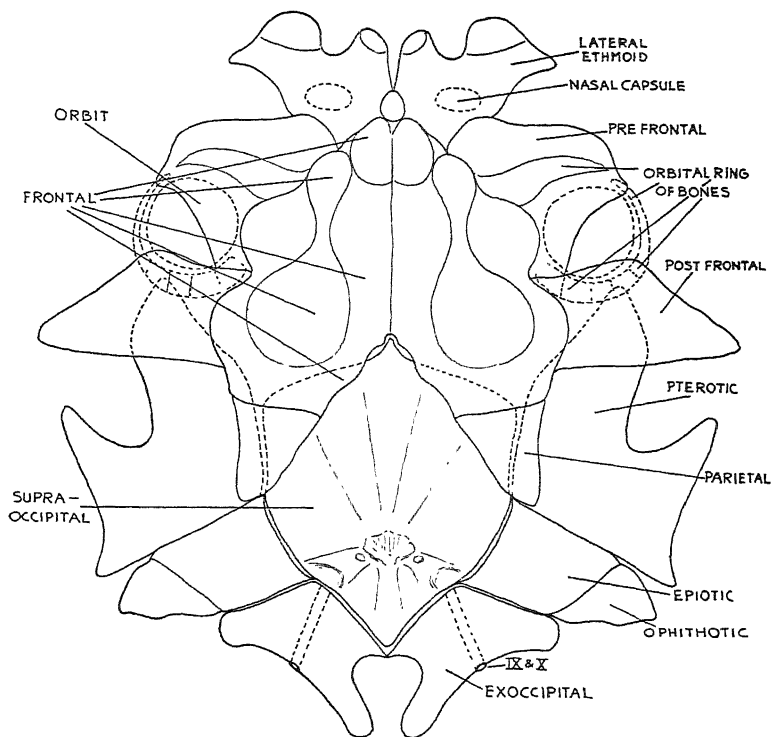
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The skeleton of this fish will be described in a series of a few papers, the first of which deals with the skull.

The general characters of the skull are :

The skull looks apparently massive from the external appearance but when dissected, individual bones which go to make the skull, are seen to be delicate and fragile and with the slightest pressure they seem to crumble to pieces when dry. The lower jaw appears to be heavier and longer than the upper one which forms the lower limit of the skull. In preserved specimens the lower jaw generally hangs down when the mouth remains open with a wide gape. In this condition the lower jaw protrudes anteriorly a little beyond the anterior margin of the skull. It may be an adaptative character. When the jaws meet, the upper jaw is locked into the lower one and small animals taken in with water passing into the mouth are easily trapped and kept there till they are pushed into the pharynx.

The gape is wider and broader owing to the fact that the Hyomandibular which is articulated with the Pterotic by a ball and socket joint and with the Post-frontal (Sphenotic) by a small flat process is longer and makes an acute angle with the lower jaw by its attachment with the Quadrate which is pushed further backward (posteriorly). The Pterygoids, Palatines and the Premaxillae are articulated one with the other and with the Hyomandibular through the Ento- and Meta-pterygoids. The ligament and the muscles which form an attachment between the Hyomandibular and the lower jaw pass over the acute angle formed between the Symplectic and the Quadrate on one side and the Articular on the other. With a slight contraction of these muscles the lower jaw goes down and the mouth widely opens to swallow disproportionately bigger prawns or shrimps, which constitute the main food of this fish.

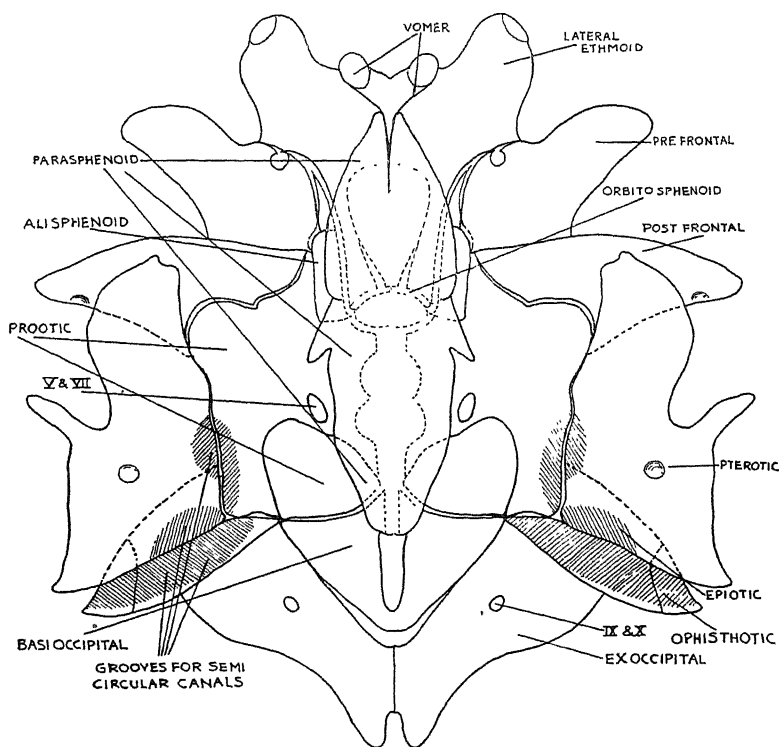


DORSAL VIEW OF THE SKULL

FIG. 1.

The skull is more or less compact, the individual bones, though fragile and delicate, being articulated with one another with a great quantity of cement of the connective tissue. The cranial chamber is small and narrow. Its roof is mainly formed by the Frontals. The Supra-occipital however covers the posterior part of the brain from the dorsal side. The Parasphenoid becomes its floor, while the side-walls are made up of the basal parts of the Pre-frontals, the Alisphenoids, the Pro-otics and the Basi-occipital. The sense capsules are poorly developed except the auditory. The eyes are apparently smaller and are a little round. They are placed far apart from each other on the external surface of the skull but their bases approach each other on their inner sides towards the cranial (brain) chamber. The skull is of the platybasic type. There does not seem to be any interorbital septum. Each orbit is formed by the bases of the Pre- and the Post-frontals and the Alisphenoids and is surrounded on the dorsal side by a ring of small bones. The Orbitosphenoids are entirely absent. The foramen for the optic nerve is formed by the crescent-shaped basal

process of the Pre-frontal backed by the Alisphenoid. The Basisphenoid is represented by a small "Y" shaped piece of a bone. Its limbs give attachment to the Alisphenoids while the median piece is attached to the ventral Median Ethmoid.



VENTRAL VIEW OF THE SKULL.

FIG. 2.

The nasal capsules are cup-shaped depressions found dorsally along the outer margins of the Lateral Ethmoids. Each capsule opens to the outside with two apertures. There does not seem to be any definite nasal bone in connection with the capsule. The internasal septum is formed by the intervening Median Ethmoid.

The auditory capsules are, however, well developed and all the otic bones appear to be present. The Pro-otics and the Pterotics are the largest bones ; while the Epiotics and the Ophisthotics are smaller and all of them together are found to accommodate the semicircular ear canals into the grooves formed along some portions of their margins facing one another. The Sphenotics are, however, a little away from the auditory capsules and do not take any part in the

formation of the same. The Sacculus with a well-developed otolith is found enclosed in a wide groove formed on the dorsal face of the Pro-otics and Basioccipital and the same is roofed over partly by the Frontals and partly by the Supra-occipital.

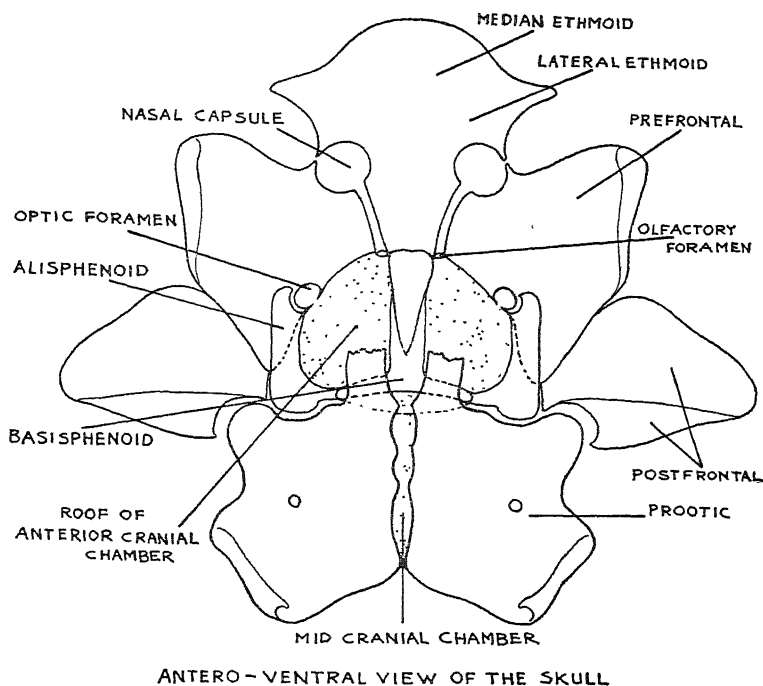


FIG. 3.

The Frontals are broader than long and meet each other along the inner mid-line, while at the anterior and posterior ends they curve a bit outward. The Parietals which are attached to the Frontals at the latero-posterior ends are separated from each other by the wedging in of the Supraoccipital.

On the ventral side the Parasphenoid forms a long and narrow boat-shaped structure but it is bent a little dorsalward in the mid-region. Into its anterior narrow and bifid end is fitted the Vomer and at the posterior margin found the Basioccipital. There is a prominent strong keel on its ventral side.

The majority of the bones of the skull can be divided into two parts—osseous and cartilaginous; the former are exposed while the latter are either overlapped by other bones and find internal attachment. The cartilaginous portion seems to exceed the osseous in bulk.

The average adult skull measures about a centimetre to a centimetre and half while its breadth at its widest plane equals its length. The skull, therefore, appears to be irregularly square, somewhat flattened dorsally with margins drawn out into long or short processes. The ventral surface of the skull, on the other hand, seems to be a bit bulging out in the middle owing to the boat-shaped Parasphenoid.

The skull is, for descriptive purposes, divided into the following parts :—The Ethmoidal, the Frontal, the Otic, the Occipital, the Suspensorial and the Mandibular.

1. *Ethmoidal region* :—The Ethmoids can be conveniently divided into two parts—the Median Ethmoid which is articulated to the Premaxillae anteriorly more or less on the dorsal side and to the Palatine and the Vomer on the ventral ; the Lateral or Ecto-ethmoids attached to the Prefrontals along the outer side and to the Palatines ventro-laterally. Dorsally the Median Ethmoid is overlapped by the Frontals while ventrally it is continued into a tongue-shaped process to which is attached the Basisphenoidal rostrum or the Basisphenoid.

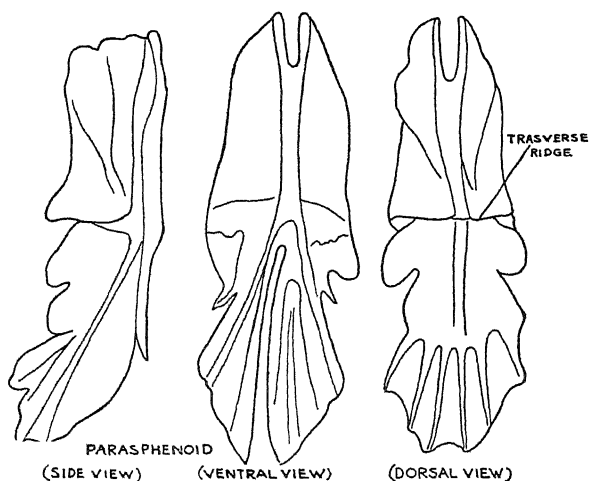


FIG. 4.

The Median Ethmoid (Fig. 3) forms an irregularly squared single structure at the anterior end of the skull. It comes in contact with the anterior boundary of the Frontals and is then continued a little distance below the Frontals and above the Parasphenoid.

At the anterior end the Median Ethmoid gives rise to two blunt and flat horns to the ventral cupshaped surfaces of which are articulated the Premaxilla and the Palatine of each side on their way to meet their final articulations. There are two flat tubercles situated

on the ventral side one on each side of the mid-line. To each of them is attached the anterior portion of the forked Vomer.

The Lateral Ethmoid (Figs. 1, 2, 3) is the lateral prolongation of the Median Ethmoid and gives attachment to the Prefrontal. On its dorsal surface is formed on each side a depression which is laterally elongated. Into this depression is found enclosed the nasal organ of that side.

The Median Ethmoid is continued below the Frontals and it forms the anterior wall of the cranial chamber. Along the floor of the latter the Ethmoid is, however, continued into a short tongue-shaped process which is articulated with the Basisphenoidal rostrum. At the antero-lateral margins of this wall are found the foramina for the olfactory nerves. The latter reach the nasal organ of each side after passing through the channel formed along the line of meeting between the Lateral Ethmoids and the Pre-frontals (Fig. 3). The nasal septum, if present, is formed by interposing of the Median Ethmoid. A bristle can however pass lengthwise through the centre of the Median Ethmoid and may therefore show the double nature of the same.

On the median postero-dorsal surface of the Median Ethmoid is found a raised swollen knob-like structure which appears to serve for the attachment of the skin covering the lateral canals in this region. This structure is found enclosed between the two Frontals at the anterior end.

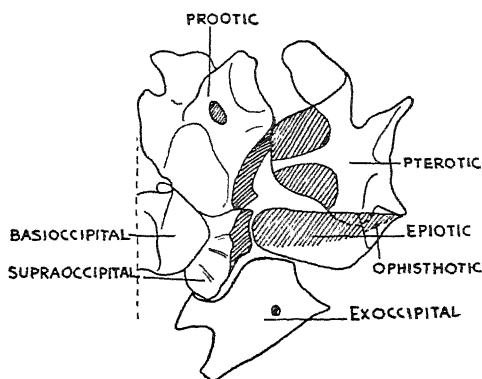


Fig. 5. Diagrammatic sketch showing inter-relations of the otic bones from the ventral side.

Vomer : (Fig. 2). It is a single forked bone found along the ventral mid-line of the skull at the anterior end. It is forked into two parts anteriorly. Each of them is swollen and becomes more or less heart-shaped at the distal end and is fused on to the flat tubercle found on the ventral surface of the Median Ethmoid. The distal swollen

portion of the Vomer is more or less concave on the ventral side and forms a shallow saucer-shaped depression into which is embedded the anterior end of the Palatine. The median common portion of the Vomer tapers gradually towards the posterior end and is wedged into the anterior bifid end of the Parasphenoid.

II. *Frontal region* : (Figs. 1, 2, 3, 4). It consists of the Frontals on the dorsal, the Parasphenoid on the ventral and the Pre- and Post-frontals and the Parietals at the sides. Besides these there are the Alisphenoids and the Basisphenoid between the Frontals and the Parasphenoid.

The Frontals : (Fig. 1). These bones are the largest and the thickest in the skull, and extend over a greater part of its dorsal surface. They are a little broader in the midregion, though they appear to be almost a square. They are slightly convex along their outer margins. Both the Frontals are connected with each other along the midline, but at the extreme anterior and posterior ends they are a little separated. In these spaces are enclosed at the anterior end the swollen knoblike structure the Median Ethmoid and at the posterior the anterior part of the Supraoccipital.

The dorsal surface of these bones is sculptured with small grooves which are arched over by delicate bony processes. Through these grooves and below the arches pass the lateral line canals.

The Frontals overlap the edges of many bones along their outer margins. At the anterior end the Median Ethmoid, along the lateral border the Pre- and Post-frontals and the Pterotic, and at the posterior end the Supraoccipital and lastly the Parietals find themselves attached to the Frontals at the postero-lateral end and are also slightly overlapped by them. To their inner surface are attached Alisphenoids, the Pro-otics and the Basisphenoid which are, therefore, completely covered over by the Frontals. The cranial chamber is roofed over by the Frontals.

The Parasphenoid : (Figs. 2-4). It is a single bone and the second longest after the Frontals. This bone is on the ventral side of the skull and extends from the base of the Vomer at the anterior to the Basisphenoid at the posterior end. As a matter of fact the Parasphenoid covers the median ventral portion of the skull and forms the floor of the cranial cavity. It is strongly boat-shaped with the prominent keel on the ventral side. It is bent a little in the middle region and both its ends are raised a little dorsalwards so that the central portion of the Parasphenoid seems to bulge out proportionately ventralwards. This bone is thin and delicate and its margins (especially the posterior) are frayed out. It is deeply bifid at

the anterior end while the posterior is more or less entire though frayed. The keel which is a raised but flat ridge with a groove in it, divides the Parasphenoid into two equal longitudinal halves, and the transverse ridge inside the hollow of the boat divides the same bone transversely again into two halves. The groove of the keel gives rise to many secondary smaller grooves towards the posterior margin of the bone. These grooves become ridges on its other side and the latter are fitted into similar grooves on the ventral surface of the Basisoccipital.

The hollow of the boat encloses wholly the tongue-shaped process of the Median Ethmoid and the Basisphenoidal rostrum, greater portions of the Alisphenoids and very small parts of the Pro-otics. The last bone is almost wholly visible from the ventral side, while a very small portion of the Alisphenoids is exposed to the outside view.

The Parasphenoid gives attachment to many bones. The processes of the pro-otics and those of the Prefrontals find their articulations along the indented lateral margins as well as on the inner surface. Into the anterior end is inserted the Vomer and at the posterior is found the Basisphenoid with its serrated margins fitted into the grooves of the Parasphenoid.



Fig. 14.

The Pre-frontals : (Figs. 1, 2, 3, 14). They are paired bones. Each of them is found situated at anterolateral side of the skull. It is more or less flat dorso-ventrally with the broader base. It is attached to the Lateral Ethmoids, the Alisphenoids and the Post-frontal. Though flat dorsally, its ventral surface is slightly concave and this concavity forms a part of the orbit. At their bases, they give rise to short and flat processes which are connected to the inner surface of the Parasphenoid. Along the outer margins of the Alisphenoids it forms a crescent-shaped incomplete foramen for the optic nerve (Figs. 3 and 14). Along the line of their articulation with the Lateral Ethmoid run the olfactory nerves (Figs. 3 and 11).

The Post-frontals : (Figs. 1, 2, 3). They are also paired bones with a strong outward process similar to that of the Prefrontal. The Post- and Pre-frontals together form the concave floor (see the Pre-frontals) on the ventral side for the accommodation of the orbits. The outward process is slightly incurved along the posterior side. Towards the base there are three articulations : anteriorly with the Prefrontals, medially with the Alisphenoids and the Pro-otics and posteriorly with the Pterotics along the incurved posterior margin.

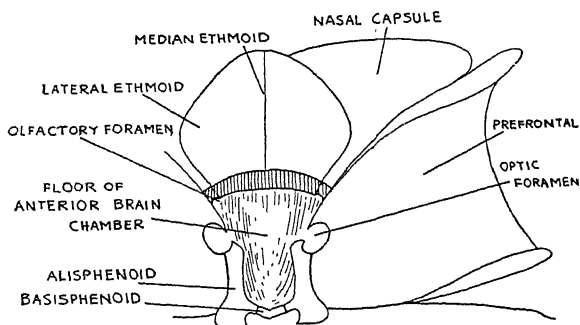


Fig. 11. Antero-dorsal view of the brain-cavity and nerves I and II.

(N.B.—Lateral Ethmoid is wrongly indicated. The portion between the Median Ethmoid and the Prefrontal represents the Lateral Ethmoid.)

On the ventro-posterior side of the Postfrontal is found a deep notch into which is fitted the head process of the Hyomandibular (see Hyomandibular).

This bone seems to be identical with the Sphenotic and it is therefore sometimes called the *Sphenotic*.

The Parietals : (Fig. 1). They are thin, flat and platelike paired bones attached to the postero-lateral margins of the Frontals. They are widely separated from each other by the intervening Supraoccipital. They are more or less triangular in shape, the base of the triangle being attached to the Frontals. One of the remaining two sides is overlapping a part of the Pterotic and the other side that of the Supraoccipital. The drawn out end of the triangle touches the Epiotic.

The Alisphenoids : (Figs. 2 and 3). The Alisphenoids are hardly visible from outside. They are completely overlapped by the Frontals from the dorsal, while they are enclosed in the hollow of the Parasphenoid on the ventral side. A very small portion of the Alisphenoid can, however, be seen from the ventral side of the skull as a thin strip between the outer edge of the Parasphenoid on one hand and the inner bases of Pre- and Post-frontals and the anterior margins of the Pro-otics on the other.

Each Alisphenoid may be divided into two parts—the stem and

the process. The basal part or the stem is more or less flat and extends a little antero-posteriorly and is attached to the inner side of the Frontal nearer the mid-line. It projects a little beyond the borders of the Parasphenoid when it is possible to see this strip. To this base are attached the basal parts of the Pre- and Post-frontals and the Pro-otics.

The process starts from the inside at about the mid-portion of the stem of the Alisphenoid. It curves inwards to meet one of the ends of the Basisphenoid (Figs. 3, 11 and 15). This part of the Alisphenoid with the Basisphenoid forms an arch below which is found lodged the anterior part of the brain. The roof of this arch is formed by the Frontals.

The Basisphenoid or the Basisphenoidal Rostrum. (Figs. 2 and 3). There is a single "Y" shaped piece of a bone attached to the distal posterior end of the tongue-shaped process of the Median Ethmoid by the median piece of the "Y". The limbs of the Y are articulated to the Alisphenoids and an arch is thus formed. This "Y" shaped Basisphenoid is embedded in the hollow of the boat of the Parasphenoid. The limbs are fused along the median transverse ridge of the Parasphenoid by their inner surface, while the median stalk of the "Y", though enclosed in the hollow of the Parasphenoid is not attached to it.

III. *Otic Region* : (Figs. 1, 2, 3, 5, 6, 7 and 8). The bones of the otic region are well developed. The sides of the Pro-otic, Pterotic, Epiotic and Ophisthotic which are adjoining one another are well excavated from inside to form grooves in order to accommodate the semi-circular canals of the internal ear.

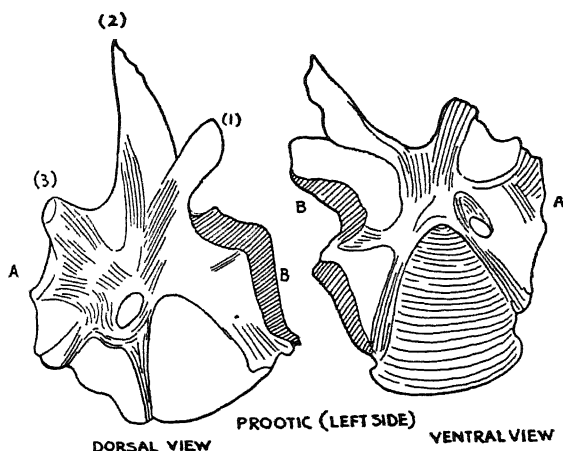


Fig. 6.

The Pro-otics : (Figs. 3, 5, 6). They are irregularly square plates of bone with a single foramen in each of them, which allows a blood vessel to pass out. On the dorsal surface there are ridges and shallow grooves. One of these grooves fits with that of the Basioccipital (Fig. 2) to form a continuous wide groove to enclose the Sacculus with the otolith. The Pro-otics of both sides come near each other along the ventral median line and are then covered over by the Parasphenoid to the sides of which they are firmly attached. The anterolateral process (1) is attached to the Alisphenoids, the anterior process (3) with the Post-frontals (Sphenotics) and the third process (2) which is longer reaches the base of the Prefrontal. The posterolateral side is excavated for the anterior vertical canal of the ear and is connected with the Pterotics. Their posterior sides meet those of the Basioccipital (Fig. 5).

On the dorsal side the Pro-otics are completely covered over by the Frontals to which they are firmly attached by their dorsal margins. On the ventral side they are slightly hidden, being overlapped by the Parasphenoid along their inner borders, while the rest of them is exposed to the view from the ventral side of the skull.

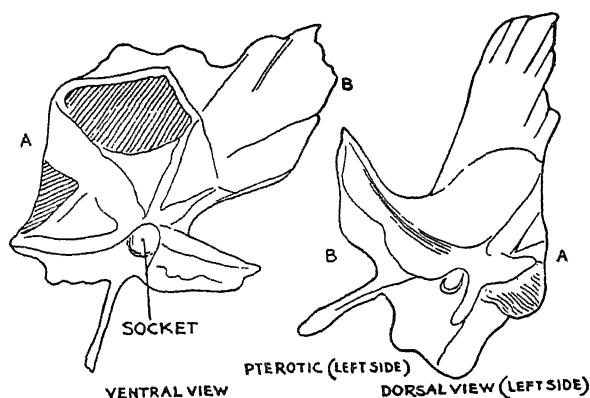


Fig. 7.

The Pterotics : (Figs. 1, 5 7). They are well developed bones giving rise to a few processes projecting some anteriorly and others posteriorly beyond the skull. Their central surface is strongly ossified and there are one or two hooklike structures for the articulations with the Supraoccipital and the Parietals. Some of these processes are useful for the attachment of the muscles of the Hyomandibular and the parts of the Pectoral girdle.

On the ventral side these bones have a conspicuous central socket into which is fitted a ball-like structure of the head of the

Hyomandibular. Along the inner margins of the Pterotics facing the Pro-otics, Supraoccipital and the Epiotics are found two wide grooves through which one of the semicircular canals passes (Fig. 5).

These Pterotics are surrounded along their anterior borders by the Pro-otics and the Post-frontals, ventrally by Pro-otics, dorsally on the inner side by the Frontals and the Supraoccipital, and posteriorly by the Epiotics. These bones are partially covered over by the Parietals.

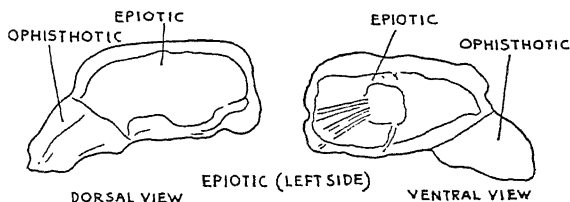


Fig. 8.

The Epiotics : (Figs. 5 and 8). They are also well developed bones. They are like the broad portion of a leaf bulging a little dorsalward and forming a sort of a hollow on the ventral side. On the inner side they are attached to the Supraoccipital by their broad bases and at their distal ends are found articulated with the Ophisthotics.

If viewed from the ventral side, the hollow is divided by a vertical wall into two parts—one longer and broader and the other narrower and tapering outside. The former is the Epiotic and the latter forms the Ophisthotic. (Figs 5, 8 and 9).

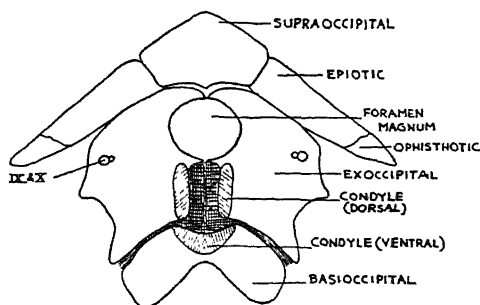


Fig. 9. Diagrammatic sketch to show the posterior-most part of the skull.

The Ophisthotics : (Figs. 5, 8 and 9). As mentioned above they are the end parts of the Epiotics. Like the latter they are convex on the dorsal side and concave on the ventral. Their outer edges follow the posterior outline of the Pterotics.

The Sphenotics : (Post-frontals). They have already been described above under the Post-frontals.

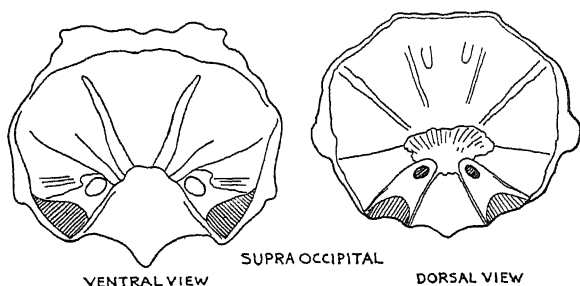


Fig. 10.

IV. *The Occipital region* : (Figs. 1, 2, 9, 10, 12). It is again the region of well developed bones forming the posterior part of the skull.

The Supraoccipital : (Figs. 1, 9, and 10). It is a single bone entirely placed on the dorsal side. It is a more or less many sided plate-like bone giving attachment to several bones. Along the anterior margin it is overlapped by the posterior margin of the Frontals and laterally by the Parietals under which it touches the Pterotics. Along the dorso-posterior margin it gives articulations to the Epiotics and ventro-posteriorly to the Exoccipitals. The Supraoccipital is convex from outside and concave from within so that it forms a caplike covering to the posterior parts of the brain. There are bony ridges on the midportion of the dorsal side, giving an appearance of a crest.

A blood vessel enters the Supraoccipital on each side and passes through the tunnel and the excavation to reach the area of the inner ear. (Fig. 10).

The Exoccipitals : (Figs. 1, 10 and 11). They are stout bones placed ventro-laterally. They form the posterior boundary of the skull.

Dorsally they touch the Supraoccipital. Their inner ends form the Foramen Magnum just below the Supraoccipital and give rise to two vertical condyles below the Foramen Magnum. The Supraoccipital is, however, excluded altogether from the Foramen. On the ventral side the Exoccipitals are articulated with the Basioccipital. Antero-laterally they meet the Epiotics.

There are two apertures, one large and one small, close to each other, for the exit of IX and X nerves (Fig. 11). Sometimes these apertures merge into each other.

The Basioccipital: (Figs. 2 and 12). It is a single median bone placed on the ventral side and at the posterior end of the skull. Its anterior margin consists of two parts; the ridged central portion which closely fits into the corresponding groove of the enveloping Parasphenoid and the lateral portion which forms a shallow and wide groove continuous with that of the Pro-otic of each side.

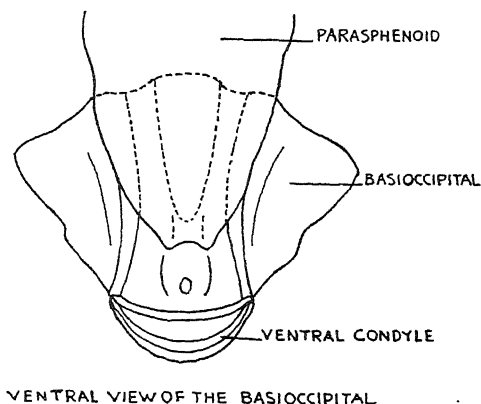


Fig. 12.

The distal end is strongly ossified and has an aperture for the spinal vessel. This part has a condyle developed ventroposteriorly. It is more or less semicircular with the strongly convex outer edge.

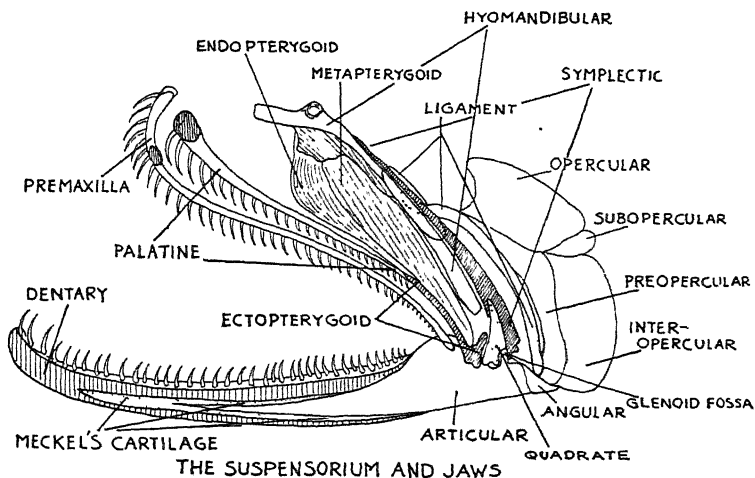


Fig. 13.

V. *Suspensoreal region* : (Fig. 13). It includes the Hyomandibular, Symplectic, Pterygoids, Palatine and lastly the Quadrate.

The Hyomandibular : The Hyomandibular is one of the longer bones in this region. It is obliquely placed making acute angles at the either ends with the posterior part of the skull and the Pterygoids and the jaws respectively. It is a compound bone formed by fusion of two bones ; the Hyomandibular proper and the Symplectic. Each component bone consists of the head and the shaft. The shafts of both the bones form a common single structure. The head of the Hyomandibular proper gives rise to two articular processes, one attached to the Post-frontal and the other to the Pterotic. The Pterotic articulation is of the nature of the ball and socket joint, while a narrow and flat process in continuation of the head fits into the depression on the ventral side of the Postfrontal. A small flat process is also found projecting from the underside, i.e., antero-Ventral surface for the articulation of the Ento- and the Metapterygoids.

The shaft is continued from the head towards the ventral side. It is flattened laterally and a deep groove is formed on the inner side. In this groove is buried the shaft of the Symplectic. Towards the Quadrate both the bones become visibly separate from each other. The head of the Symplectic is fused with the Quadrate and the Hyomandibular end with Epi- (stylo-) hyal.

To the outer side (that is the postero-dorsal) of the Hyomandibular proper is fused a ligament to which are attached the Opercular bones.

The Symplectic : (Fig. 13). This bone seems to be quite different in shape from a similar bone in other fish. In the latter case it is a small bone attached to the distal end portion of the Hyomandibular. In this fish, on the other hand, it is a long bone attached lengthwise with the Hyomandibular proper on the inner side, while its knoblike distal end is fused with the outer margin of the Quadrate to form the Glenoid fossa. The distal portion of the Symplectic is pierced by a nerve and a vessel which enter the same from the Hyomandibular side and emerge just before its articulation with the Quadrate.

The Symplectic tapers gradually to a small splinter towards the dorsal end when it is longitudinally fused with the Hyomandibular proper.

Pterygoids : (Fig. 13). There are three different pieces of bones between the Hyomandibular on one side and the Premaxilla on the other. They are Ectopterygoid (Pterygoid), Meso-(Ento) pterygoid and lastly Meta-ptyerygoid.

(a) Ectopterygoid. It is a narrow cylindrical bone without any teeth. It is fused with the Quadrate along the inner side and is

situated just inside the Premaxilla. It is, however, quite distinct from the latter. It runs anterodorsally for a short distance when it is articulated with the Palatine.

(b) Meso (Ento) pterygoid which lies between the Ectopterygoid and Metapterygoid is a thin plate-like structure. It is attached by both of its margins one with the Ecto and the other with the Metapterygoid while the distal end is fused with the winged expansion of the Hyomandibular proper near its head.

(c) Metapterygoid. It is almost similar in shape to the Meso (Ento) pterygoid. It is articulated by the inner and the outer margins with the Entopterygoid and the Hyomandibular proper respectively.

Ento- and Metapterygoids do not reach the Quadrate.

The Palatines : Each Palatine is a more or less cylindrical and long bone. It curves slightly inwards while passing along the antero-ventral boundary of the skull. It is attached to the Ectopterygoid at one end and from its attachment onwards it begins to bear along the Vento-lateral side a double row of long curved teeth. It is separated from the Entopterygoid by a thick pad of a connective tissue and muscles. It is articulated with the Vomer at the other end on the ventral side of the skull. This end portion of the Palatine is knob-like and is fitted into the cup-shaped head of the Vomer. At this end the teeth longer and strongly hooked.

It is articulated on its way to the Vomer with the Premaxilla by a facet at the place where this bone is bent inside. The place of articulation becomes a little flattened out on the ventral side to which the Premaxilla is attached by a connective tissue.

The Quadrate : (Fig. 13.) It is a small irregular bone. It is more or less wedge-shaped. The Symplectic is fused on the outer side and the Ectopterygoid on its inner side. The distal extremity of the fused Quadrate and the Symplectic forms the Glenoid fossa from which the Ectopterygoid is excluded.

Opercular Bones : The Opercular bones will be described with the Visceral Arches in a separate paper.

VI. *The Jaws* : They consist of the upper and lower jaws.

The Upper Jaw : It is mainly formed by a single bone of the Premaxilla. The maxilla is not present and if considered to be present, it must be so completely fused with the Premaxilla that it cannot be separated from it.

The Premaxilla is a cylindrical bone following closely the latero-anterior contour of the skull. It is a long, slender and curved bone. It is a little compressed laterally towards the anterior end. The two Premaxillae articulate with each other in the middle line at the anterior-most point of the skull. This articulation is effected by means of a connective tissue. At the other end each Premaxilla is fused on to the Coronoid process of the Articular. This end is thin and tapering, while the other end flattened a little from side to side.

Between these two end articulations, there are two more : one with the Palatine and the other with the Median Ethmoid.

It bears long curved teeth on inner lateral surface.

The Lower Jaw : It is made up of three pieces of bones, the Articular, Angular and Dentary.

(a) *The Articular* : It can be divided into the head and two anterior processes. The head bears a knoblike structure which fits into the Glenoid fossa of the Quadrate.

The anterior processes are in the form of a fork arising from the common stalk continued from the head. They are dove-tailed into the similar processes of the Dentary. One of the limbs of the former is wedged from outside into the fork of the Dentary. The other limb is on the inside of the latter.

Nearer the head, the upper (dorsal) portion of the stalk is expanded and forms a more or less semicircular flat structure. It is known as the Coronoid process of the Articular and the Premaxilla is fused on to this process.

(b) *Angular* : This is a small, almost completely cartilaginous piece of a bone of a triangular shape. It is attached to the posterior border of the Articular. To its distal end is fused the opercular ligament.

(c) *Dentary* : The last portion of the Lower Jaw is the Dentary. Like the Articular it forms a fork at the distal end from the anteriormost common stalk. Between the limbs of the fork are inserted the processes of the Articular and in between the forks of the Dentary and the Articular is found the Meckel's Cartilage.

The uppermost limb of the fork reaches the Coronoid process of the Articular and fuses with it. It bears curved long teeth along the whole dorso-lateral surface. The two Dentaries are fused with each other below the Premaxillae but a little further up so that the lower jaw seems to be longer, more protruding anteriorly and more hook-shaped than the upper.

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